ROLE OF BIODIESEL WITH NANOADDITIVES IN PORT OWNED TRUCKS AND OTHER VEHICLES FOR EMISSION REDUCTION

by

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Biodiesel is presently available all over the world and can be produced from several types of biomass. Biodiesel fuels are gaining more and more importance as an attractive alternate fuel in various transport sectors due to their renewable nature and lower pollution impact. However, the ports and the shipping sector are still in the early stage of orientation towards biofuels. In the present work, an experimental investigation on the use of diesterol blend (a mixture of diesel, ethanol with biodiesel) with cerium oxide as a nanoadditive (D80JBD15E4S1 + cerium oxide) in a compression ignition engine is performed to assess the emission characteristics. The results reveal that the presence of the cerium oxide nanoparticle changes the reaction patterns and heat transfer rate that reduces both the CO and CO_2 percentage concentration in the exhaust gas appreciably. Further, the reduction in CO_2 emission in the port of Chennai is quantified considering the replacement of neat diesel with those of modified diesel blend in port owned trucks and vehicles.

Key words: *diesterol, cerium oxide, green port, biodiesel, nanoadditive*

Introduction

Depletion of fossil fuels and environmental degradation are the two major issues being faced in the present scenario. The growth of a country is linked with the availability of fuels for transportation and power generation. Today fossil fuels occupy up to 80% of the primary energy consumed in the world, of which 58% is consumed by the transport sector. Figure 1 indicates the global energy consumption in transport sector accounted for approximately 2200 MTOE of which 10% is consumed by global marine sector. It is predicted that the world consumption of petroleum-based fuels would reach 118 million barrels per day in 2025 [1]. Increasing energy demand leads to increasing crude oil price which may directly affect the global economic activity. According to International Energy Agency, India would become the fourth largest importer of oil in the world by 2025, behind the United States, China, and Japan. Thus, the world faces the major challenge of high oil demand to meet the growing energy needs. One of the major threats in view of the environmental standpoint is the emis-

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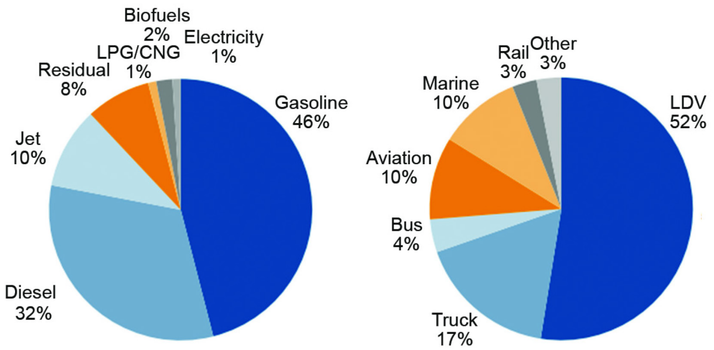

Figure 1. Energy consumption in transport sector by source and by mode – year 2011 (total ~2,200 MTOE) [2]; LPG – liquid petrol gas, CNG – compressed natural gas, LDV – light duty vehicle

sion due to combustion of petroleum-based fuels. The use of conventional fossil fuels results in climate change, which might lead to ecological disasters around the globe.

In recent years, emissions from compression ignition (CI) engines are a serious threat to the environment and are considered as one of the major sources of air pollution. Hence, emission control has become the major driving force in the development of CI engines. It is commonly accepted that clean combustion of Diesel engines can be fulfilled only if the engine development is coupled with diesel fuel reformulation or additive introduction. Hence, it is important to reconnoiter alternative, renewable, sustainable, and cost-effective sources which can be generated within the country on a large scale for commercial utilization. Biodiesel fuels are gaining more importance as an attractive alternative fuel in the recent years in several sectors.

In the present scenario, there is a huge promotion given by the Government of India to convert the existing ports into green ports. Recently, Haldia port has been converted into green port. Railway engines, trucks, and other vehicles in the port, India are being operated on biodiesel. The port has eight oil refineries for imported palm oil from Malaysia and it has been using its residue to manufacture 300,000 liters of biodiesel. The use of biofuels not only is a strong option to realize lower carbon intensity in the propulsion of ships but also shows potential to reduce the pressure of ship emissions on local air quality. A 100% biofuels show no sulphur content. Biofuels, in 100% blends, can even have a health, safety, and security environment benefits in case of spills to the marine environment due to their biodegradable nature, compared to conventional marine fossil fuels. So, biofuels are a good sustainable alternative for fossil marine fuels. The most commonly used marine fuels and their properties are as shown in tab. 1. Among the many biofuels, ethanol and biodiesel (vegetable methyl esters) are considered as a most suitable fuel extender and fuel additive due to its high oxygen content and renewable nature.

Over the past years, extensive research has been carried out in analyzing the performance and emission characteristics of a Diesel engine by using diesel-biodiesel blend by varying the proportions. The use of a diesel-biodiesel blend fuel reduced the total HC and CO emissions but increased nitrogen oxide (NO_x) emissions due to the increased oxygen content in the fuel reported by [3-5]. Jain *et al.* [6] reported the technical disadvantages of biodiesel/fossil diesel blends include problems with fuel freezing in cold weather, reduced energy density, and the degradation of fuel under storage for prolonged periods. Among the several techniques to reduce exhaust emissions, the use of fuel-borne catalyst was primarily focused due to its advantage of the increase in fuel efficiency while reducing harmful greenhouse gas emissions. The influence of cerium oxide (C_eO_2)additive on ultrafine diesel particle emissions

Table 1. General specification of most common marine fuels and selected biofuels (source: ECOFYS report)

Fuels	Cetane number	Gross calorific value [MJkg^{-1}]	Kinematic viscosity [mm^{2}s^{-1}] at 40 °C	Cloud point [°C]	Pour point [°C]	Flash point [°C]	Density at 15 °C [kgm^{-3}]
Diesel	40-55	44-70	2.61	–5	–6	65	820-860
Straight vegetable oil	37-42	39.5-39.7	32-37	–4-7	–32- –12	246-274	900
Raw pyrolysis bio-oil	10	22.7	14.5	–21	–33- –12	40-100	1100-1250
Biodiesel	49-58	37.3-39.8	4.2-4.5	–1-8	–4-6	110-195	880-920
Di-methyl ether	55-60	29.8	0.2-0.25	unknown	unknown	–41	665
Bio-methane	–	55	n/a	n/a	n/a	–188	0.66
Bio-ethanol	8	29.8	1.2	n/a	n/a	12	791

and kinetics of oxidation was studied by Jung *et al.* [7]. They found that inclusion of cerium to diesel caused a major reduction in number weighted size distributions and light-off temperature and the oxidation rate was increased significantly. Ribeiro *et al.* [8] discussed the oxidation stability of biodiesel. The esters of unsaturated fatty acids are unstable with respect to light, catalytic systems, and atmospheric oxygen. It is one of the key issues in using vegetable oil based fuel, and attention is given to the stability of biodiesel during storage and use.

These problems could be circumvented by using additives. Hence, conventional liquid fuels with the addition of energetic nanoscale materials* as fuel additives to enhance the performance and emission characteristics in a CI engine is an interesting and novel concept. The recent advancements in nanotechnology have a large impact in several applications. Nanomaterials are used to produce either novel or enhanced physical properties. In recent years, scientists and researchers have applied nanotechnology to the field of fuel engineering. Wen [9] considered energetic nanoparticles/nanoenergetic or suspensions of energetic nanoparticles in a liquid carrier, as a secondary energy carrier. One of the methods to vary the specific fuel properties and combustion of a liquid fuel is the use of nanoadditives. Nanofluid fuel is a new class of fuel with the suspension of nanoscale sized particles [10]. These fuels are known to exhibit different thermophysical properties when compared to conventional liquid fuel.

In this direction, Shaafi *et al.* [11] critically reviewed the effect of dispersion of various nanoadditives on the performance and emission characteristics of a CI engine fueled with diesel, biodiesel, and blends. Recently, Shaafi and Velraj [12] attempted to study the emission characteristics of the two modified fuel blend namely B20, D80SBD15E4S1 + alumina and compared with that of neat diesel. They observed a considerable reduction in the major pollutants such as CO, CO_2, and unburnt hydrocarbon (UBHC) in the case of D80SBD15E4S1 + alumina fuel blend compared to neat diesel at full load condition. The authors concluded that alumina nanoparticles enhance the NO_x emissions, due to the maximum cylinder pressure and higher heat release rate was achieved during the combustion process. Balaji and Cheralathan

* Nanoenergetic materials can store more energy than conventional energetic materials and can be used in innovative ways to tailor the release of this energy. Thermobaric weapons are one potential application of nanoenergetic materials.

[13] performed an experimental investigation to study the influence of alumina oxide (Al_2O_3) nanoadditive on the performance and emissions of a methyl ester of neem oil-fueled direct injection Diesel engine. The AL_2O_3 nanoparticles are mixed in various proportions (100 to 300 ppm) with the methyl ester of neem oil and the influence on the performance and emissions at various loads are reported. It is observed from the literature that, the combustion behavior of conventional liquid fuels with the addition the energetic nanoscale material fuel additives enhance combustion and engine performance, and control emission characteristics in a Diesel engine that provides an interesting concept for study. Considering the aforementioned, the present research investigates the effect on engine emission characteristics of the diesterol blend with CeO_2 fuel and a comparison is made with neat diesel which is highly suitable for port and shipping sectors. The obtained results are very encouraging and reported in detail in this paper.

Preparation of modified fuel blend and its properties

In the present study, the modified fuel blend consists of a mixture of 80% diesel, 15% jatropha biodiesel, 4% ethanol, and 1% isopropanol as a surfactant, and cerium oxide nanoparticles of 100 mg/L. The commercially available CeO_2 nanoparticles of size 15-30 nm, procured from M/s Alfa Aesar Karlsruhe, Germany, was used as additives in the present investigation. Its surface area is 30-50 m^2/g. Jatropha biodiesel was procured from M/S Jatropha Oil Seed Development & Research, Hyderabad, India. Two-step method was used for the preparation of the modified fuel blend. Initially, 100 mg of CeO_2 nanoparticles was mixed in ethanol (99.9% purity) and then, mixed with the diesel-jatropha biodiesel blend. The phase separation is prevented by the addition of isopropanol as a surfactant in the aforementioned fuel blend. The fuel sample was transferred to the ultrasonic agitator to thoroughly disperse the particles and to reduce their agglomeration.

The two-step method works well for oxide nanoparticles reported by [14-17]. The schematic diagram of the modified fuel prepared by the two-step method is shown in fig. 2. The fuel properties of neat diesel, D80JBD15E4S1 + CeO_2 fuel blend was determined at M/s Italab Private Limited, Chennai, India. Standard ASTM test procedures were followed in the experiments. Table 2 lists the properties of pure diesel, jatropha biodiesel, and diesel-jatropha biodiesel-ethanol blended with CeO_2 used in the present investigation.

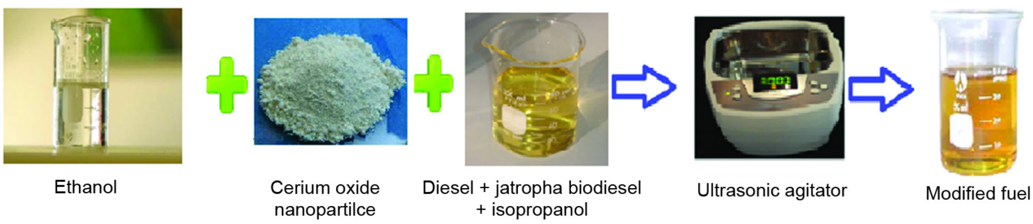

Figure 2. Schematic diagram of the modified fuel prepared by the two-step method

It is seen from tab. 2 that the specific gravity and viscosity increases in the D80JBD15E4S1 + CeO_2 fuel blend compared to neat diesel, due to the presence of the jatropha biodiesel. As the calorific value of the jatropha biodiesel is lesser than that of neat diesel, the blend mixtures show a decrease in the calorific value in proportion to the percentage mixing of the biodiesel.

Table 2. Properties of the fuel blend

Fuel property	Diesel	Jatropha biodiesel	D80JBD15E4S1+CeO_2 fuel blend
Specific gravity	0.825	0.873	0.832
Viscosity at 40 °C (cSt)	2.61	4.80	2.77
Calculated cetane index	57	54	52
Calorific value [$MJkg^{-1}$]	44.70	40.76	42.76

Experimental set-up

The schematic diagram of the experimental set-up is shown in fig. 3. A stationary single cylinder Diesel engine is used in this investigation, and its specifications are given in tab. 3.

The AC generator is used to apply the load on the engine. The load on the engine could be varied by the resistance load bank using a rheostat. An orifice meter is connected to an air surge tank which is used to measure the air consumption by the engine. The fuel tank is mounted on an electronic weighing balance and the fuel consumption rate is measured by the time taken for the consumption of 10 grams of fuel, which is monitored by the reduction in the fuel weight shown by the electronic balance.

Table 3. Engine specifications

Make and model	Kirloskar TAF1
Type	4-stroke, single cylinder, direct injection, air cooled
Bore × stroke [mm]	87.5 × 110
Compression ratio	17.5:1
Engine capacity	0.661 liter
Rated power	4.4 kW
Rated speed	1500 rpm (constant speed)
Start of injection	23° bTDC

A k-type thermocouple is mounted on the exhaust pipe to measure the exhaust gas temperature, which is used as a reference temperature to analyze the variation in the temperature in the combustion chamber. The AVL make pressure transducer and a crank

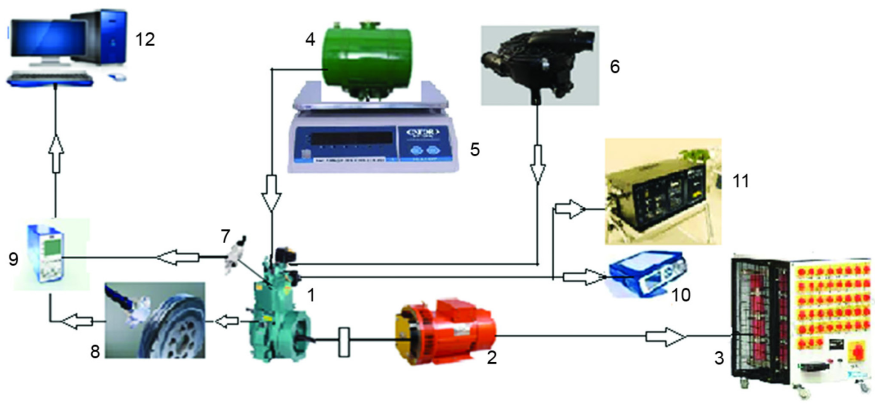

Figure 3. Schematic diagram of the experimental set-up; *1 – Diesel engine, 2 – AC generator, 3 – resistive load bank, 4 – fuel tank, 5 – electronic weighing balance, 6 – air surge tank, 7 – pressure sensor, 8 – crank angle encoder, 9 – charge amplifier, 10 – exhaust gas analyzer, 11 – smoke meter, 12 – personal computer*

Table 4. Resolution of the instruments for the measured parameters

Name of the instrument	Emission parameter	Resolution
AVL 444 Di-Gas analyzer	CO	±0.01%
	CO_2	±0.1%
	NO_x	±1 ppm
	UBHC	±1 ppm
AVL 437C smoke meter	Smoke opacity	0.001 FSN or 10 $\mu g/m^3$

angle encoder was used to measure the in-cylinder gas pressure and the corresponding crank angle. The AVL 437C smoke meter is used to measure the smoke opacity. The AVL 444 Di-Gas analyzer was used to measure the concentration of the emission parameters. The resolutions of the instruments for various measurements are given in tab. 4. A computerized data acquisition system is used to collect, store, and analyze the data during the engine testing.

To begin with, the engine is started and allowed to run for 45 minutes until it is stabilized. The engine is fueled with diesel, and then with diesterol blend with CeO_2. Under steady-state conditions, the fuel consumption rate, air consumption rate, constituents of exhaust gas, the temperature of exhaust gas, and parameters of combustion were recorded at various loads starting from the no load condition to the full load one. The engine is operated for 15 minutes at each load to stabilize it. During the experiment, it was ensured that the lubricating oil temperature did not exceed 90 °C. To ensure the repeatability of the measurement under each load, the experiments were carried out two or three times.

Results and discussion

The operation of the engine was found to be very smooth throughout the rated load, without any operational problems for the D80JBD15E4S1 + CeO_2 fuel blend. The effect of emission characteristics of the engine fuelled with D80JBD15E4S1 + CeO_2 fuel blend is discussed and compared with those of neat diesel. The carbon emission reduction potential in the port of Chennai is also quantified due to the replacement of neat diesel with 20% biodiesel.

The exhaust gas temperature is an indication of the performance of the engine and certain pollutants. The major pollutants measured, such as NO_x, UBHC, CO, and CO_2, and smoke opacity are presented and discussed in this section. The variation of exhaust gas temperature for the neat diesel and diesterol blend with CeO_2 nanoadditives at various loading conditions is shown in fig. 4. The uncertainty involved in the temperature measurement is ±0.15 °C.

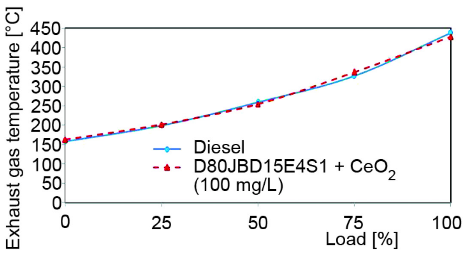

Figure 4. Variation of exhaust gas temperature with engine load, measurement precision: ±0.15 °C

It is seen from the figure that the exhaust gas temperature for both the fuels tested increase with an increase in load, due to the increased quantity of fuel burnt, that liberates more heat at higher loads when compared to lower loads. The combustion performance suggests that the maximum heat release rate was in the case of D80JBD15E4S1 + CeO_2 fuel blend, and hence, the exhaust gas temperature also should have been higher. However, the figure shows that the exhaust gas temperature is very close to the neat diesel at all loads. This is due to the higher heat transfer coefficient involved in the products of combustion with the engine cylinder, due to the presence of the nanoparticle in the products of combustion.

The NO_x are one of the important emissions in CI engines. The NO_x contains the nitric oxide and nitrogen oxide. The variation of NO_x emission for neat diesel and D80JBD15E4S1 + CeO_2 fuel blend are presented in fig. 5. It is seen from the figure that the NO_x emission is lower for the D80JBD15E4S1 + CeO_2 fuel blend at part load condition. However, beyond 50% of the load the NO_x emission is high for D80JBD15E4S1 + CeO_2 fuel blend when compared to neat diesel due to the increase of engine load nitric oxide formation increased because of the rise in peak temperature of combustion. The magnitude of NO_x emission observed at full load is 1792 ppm for neat diesel, whereas it is 1823 ppm for D80JBD15E4S1 + CeO_2 fuel blend. An increased emission of 1.72% was observed in the case of D80JBD15E4S1 + CeO_2 fuel blend at full load condition when compared to neat diesel.

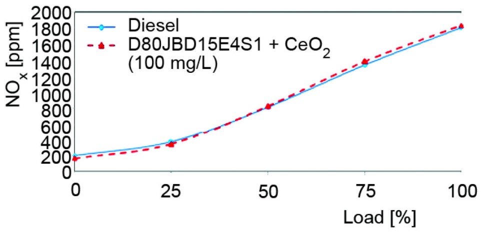

Figure 5. Variation of volume concentration of No_x emission with engine load, measurement precision: ±1 ppm

The smoke opacity of the two fuels at different loads is shown in fig. 6. The smoke opacity that increases with load reaching a maximum at full load for the fuels tested. The D80JBD15E4S1 + CeO_2 fuel blend shows the highest smoke opacity at all loads compared to diesel. This is due to the atomized fine nanoparticles which have the tendency of high dispersion that increases the percentage level of opacity in the emission.

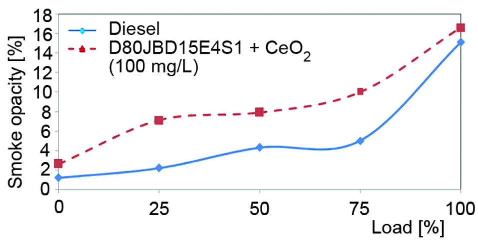

Figure 6. Variation of smoke opacity with engine load, measurement precision: 0.001 FSN or 10 μg/m³

The CO is an intermediate combustion product and CO in the exhaust gas is an indication of incomplete combustion. The variation of CO with respect to rated load for the tested fuels is shown in fig. 7. It is seen from the figure that the CO emissions of D80JBD15E4S1 + CeO_2 fuel blend, are much lower compared to the neat diesel at all loading conditions. The CO emission is lower for D80JBD15E4S1 + CeO_2 fuel blend by 33.33% at part load (no load and 25% load) compared to neat diesel and reduces at full load to the extent of 40% compared to neat diesel. The presence of the nanoparticle enhances the atomization rate that leads to complete combustion of the fuel. If the measurement precision is also considered there could be an uncertainty in the mentioned conclusion.

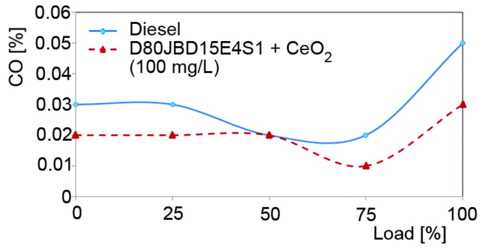

Figure 7. Variation of CO volume concentration in the exhaust gas with engine load, measurement precision: ±0.01%

The CO and UBHC production mainly depends on the mixture strength such as oxygen quantity and viscosity of the fuel. Figure 8 shows the variation of the UBHC at various loads for the two fuels considered in the analysis. It is seen from the figure that in the case of neat diesel there is a slow and uniform increase of UBHC as the load increases. In the case of

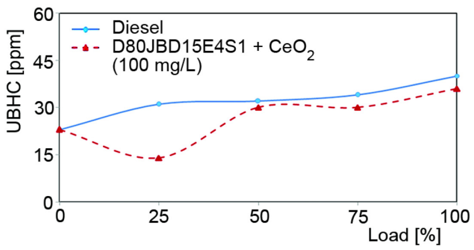

Figure 8. Variation of UBHC volume concentration with engine load, measurement precision: ±1 ppm

D80JBD15E4S1 + CeO_2 fuel blend, there are small fluctuations in the UBHC at part load condition. However, the presence of UBHC is lower in the case of D80JBD15E4S1 + CeO_2 fuel blend compared to the neat diesel at all loads. This is due to the ability of CeO_2 to undergo a transformation from the stoichiometric CeO_2 (+4) valence state to the Ce_2O_3 (+3) state *via* a relatively low energy reaction. The CeO_2 supplies the oxygen for the reduction of the HC as well as the soot and gets converted to cerous oxide (Ce_2O_3) as follows. Equations (1) and (2) show the CeO_2 involved in the HC combustion:

– hydrocarbon combustion

$$(2x + y)CeO_2 + C_xH_y \rightarrow \frac{2x + y}{2} Ce_2O_3 + \frac{x}{2} CO_2 + \frac{y}{2} H_2O \qquad (1)$$

– soot burning

$$4CeO_2 + C_{soot} \rightarrow 2\, Ce_2O_3 + CO_2 \qquad (2)$$

The CeO_2 lowers the carbon combustion, activates temperature and thus enhances HC oxidation, promoting complete combustion.

The concentration of CO_2 emission for the fuels tested under different loading conditions is presented in fig. 9. It is observed from the figure that the CO_2 variation is nearly same for the two fuels considered. At part load condition, the CO_2 concentrations, for neat diesel and D80JBD15E4S1 + CeO_2 fuel blend are identical in nature. However, as the load increases, beyond 50% the CO_2 concentration in the case of D80JBD15E4S1 + CeO_2 fuel blend is slightly lower than that for neat diesel. The reduction in CO and UBHC percentage with nanoadditive should increase the CO_2% in the exhaust due to complete combustion. However, the reduction in CO_2% at full load could be due to the lower carbon content in the biodiesel, which consumes less air for combustion compared to neat diesel.

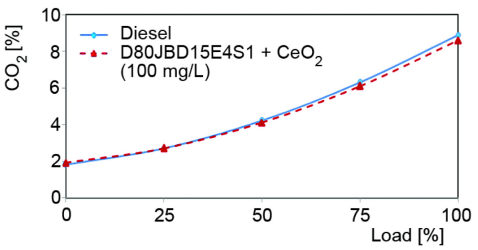

Figure 9. Variation of CO_2 concentration in the exhaust gas with engine load, measurement precision: ±0.1%

The port of Chennai, with a *go green* strategy, considers the use of biodiesel in its transport vehicles to reduce the carbon footprint. It is proposed to use the blends of 20% biodiesel in diesel equipment with no or only minor modifications to engines, thereby significantly reducing the investment costs. In addition to the CO_2 emission reduction with the use of nanoadditives in the biodiesel, since the biodiesel is carbon neutral, it is considered that there will be a reduction in CO_2 emission in proportion to the percentage of biodiesel mix with the neat diesel. As a first step, it is proposed to use B20 (20% biodiesel, 80% petroleum diesel) in all the port owned transport vehicles, which would replace nearly 28.4 kL of diesel, thereby offsetting 76.2 tones of CO_2 emissions. This is also in accordance with India's National Policy on Biofuels, which proposed a target of 20% biofuels blending (both biodiesel and bioethanol) in transport fuels, by 2017.

Conclusions

Recent advancements in nanotechnology have led to a search for suitable nanoadditives as catalysts that can appreciably reduce emissions from Diesel engines. In this direction, an attempt is made in the present research to study the combustion, engine performance, and emission characteristics of the two modified fuels prepared, and a comparison is made with neat diesel. The results are very encouraging and reported in detail in this paper. Some of the salient results are summarized.

- The presence of the CeO_2 nanoparticles changes the reaction pattern and heat transfer rate that reduces the CO_2 percentage in the emission pattern.
- The decrease in concentration of CO, CO_2, and UBHC in the case of D80JBD15E4S1 + CeO_2 fuel blend compared to neat diesel is due to the presence of O_2 in the fuel blend and the complete combustion achieved due to the presence of nanoparticles. Hence it is concluded that the amount of air required for the combustion could be reduced with this fuel blend compared to neat diesel.
- The replacement of 20% neat diesel with biodiesel in all the port-owned transport vehicles at Chennai would replace nearly 28.4 kL of diesel, thereby offsetting 76.2 tones of CO_2 emissions. Further if it is possible to quantify the reduction in the quantity of air required to achieve the similar emission pattern with diesel, the additional benefit of offsetting the CO_2 emission could be evaluated.

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