ISSN: 2321-2152

IJMECE

International Journal of modern electronics and communication engineering

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IJMECE
International Journal of modern electronics and communication engineering

ISSN2321-2152www.ijmece .com
Vol 6 Issuse.3 July 2018

Experimental Investigations on the Effects of Cerium OxideNanoparticle Fuel Additives on Biodiesel

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Abstract

This paper reports the results of experimental investigations on the influence of the addition of cerium oxide in the nanoparticle form on the major physicochemical properties and the performance of biodiesel. The physicochemical properties of the base fuel and the modified fuel formed by dispersing the catalyst nanoparticles by ultrasonic agitation are measured using ASTM standard test methods. The effects of the additive nanoparticles on the individual fuel properties, the engine performance, and emissions are studied, and the dosing level of the additive is optimized. Comparisons of the performance of the fuel with and without the additive are also presented. The flash point and the viscosity of biodiesel were found to increase with the inclusion of the cerium oxide nanoparticles. The emission levels of hydrocarbon and NOx are appreciably reduced with the addition of cerium oxide nanoparticles.

Introduction

Although diesel engines are generally more efficient than spark ignition engines, emissions from the diesel engine are typically higher. This has resulted in a somewhat negative impact on its wide acceptance and use, especially in auto- motive applications. Recently, stringent emission legislation has been imposed worldwide on the oxides of nitrogen (NOx), and smoke and particulate matter emitted from automotive diesel engines. Neeft et al. [1] have reviewed the background of the emission of particulate matters and have suggested several measures for reducing particulate and NOx emissions, such as optimizing the fuel composition, engine modifications, after-treatment techniques like selec- tive catalytic reduction of NOx with hydrocarbons and use of particulate traps. The major problem associated with particulate traps is the plugging which calls for periodic regeneration [2, 3].

The various fuel properties which affect particulate emis- sions such as the volatility, density, and the sulfur content in the fuel can be altered by the use of fuel additives. The fuel injection and mixture preparation processes are strongly influenced by properties such as the density, volatility, and viscosity, which are often interdependent.. The low temperature characteristics of diesel have more significance in relation to fuel handling than its combustion behavior. Therefore, acceptable levels must be found for appropriate physicochemical properties in order to optimize the process of combustion as well as to ensure safehandling of the fuel.

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than copper, magnesium, or calcium. Emission measurements with manganese as a fuel additive demonstrated that O_2 and CO could be decreased by 0.2% and 14.3%, respectively, SO_2 emission could be reduced, and the overall impact of all these effects was found to lead to an increase of 0.8% in the net operating efficiency.

Valentine et al. [6] experimentally observed that bimetal- lic platinum and cerium diesel fuel borne catalyst reduces the engine emissions and improves the performance of the diesel particulate filter. Shi et al. [7] reported that the particulate matter emission decreases with increasing oxygenate content in the fuels, but nitrogen oxides emissions increase. De et al.

[8] experimentally observed that the presence of ethanol and ethyl ter-butyl ether (ETBE) significantly alters the characteristics of volatility and reduces the Cetane number, impairing the fuel's performance in engine tests. The effect of methanol-containing additive (MCA) on the emission of carbonyl compounds generated from the diesel engine was studied by Chao et al. [9] and it was observed that the emission factors for some of the carbonyl compounds with the use of MCA are higher than the values for those withoutthe use of MCA.

Metal oxides such as those of copper, iron, cerium, and cobalt have been extensively used as fuel additives. The effectof cerium on the size distribution and composition of dieselparticulate matter has been studied by Skillas et al. [10], indicating a reduction in the accumulation mode, but an increase in ultrafines. Lahaye et al. [11] studied the effect of cerium oxide on soot formation and postoxidation and observed that the soot yield is not affected significantly by the presence of cerium oxide in the fuel for given oxygen content. Based on experiments, Jung et al. [12] observed that the addition of cerium to diesel fuel causes significant changes in the number concentration of particles in the accumulation mode, light off temperature, and the kinetics of oxidation. Even though the oxidation rate increased significantly with the addition of cerium to the fuel, the dosing level was found not to have much influence [12, 13].

With fossil fuels getting depleted, a number of investigations are being undertaken on alternate fuels like bio diesels derived from various natural sources such as vegetable oils. Use of biodiesel and its modifications has been reported extensively in the literature. It has been reported that singlefuel operation with neat Jatropha oil in diesel engine resulted in a slightly reduced thermal efficiency, higher HC and CO emissions as compared to diesel [14, 15]. Using a Jatropha oil-methanol blend as in place of neat Jatropha oil resulted in a slight increase in the brake thermal efficiency, a significant reduction in the exhaust gas temperature and a reduction of HC and CO emissions [16]. Experimental investigations have been reported to evaluate the effect of anticorrosion additive in palm oil-based biodiesel on the engine performance, emissions, and wear characteristics [17].

The present experimental study is aimed at investigating the effect of the use of a fuel additive in the form of cerium oxide nanoparticles on the physicochemical properties of bio diesel, and its influence on the engine performance and emissions. Cerium oxide has the ability to act as oxygen buffer causing simultaneous oxidation of hydrocarbons as

well as the reduction of oxides of nitrogen, thus reducing emissions, especially in the stoichiometric conditions. Metal-doped cerium oxide used in the nanoparticle form is proven to give much better results in efficiency enhancement compared to larger dimension powders. This technique has been evaluated in diesel fuels [18], though extensive parametric studies have not been reported. One of the major reasons for the efficiency improvement is inferred to be the high surface-to-volume ratio of nanoparticles compared to conventional powder form, as catalysis is essentially a surface phenomenon.

As important as the efficiency enhancement are the influences of additives on the emission behavior and the physicochemical properties of the fuel. Cerium oxide nanoparticles could possibly exhibit high catalytic activity because of their large surface area per unit volume, leading to improvement in the fuel efficiency and reduction in the emissions. With this background, extensive investigations on the performance as well as emissions and physicothermal properties of bio diesel with the inclusion of pure cerium oxide in the nanopowder form suspended in the fuel by an ultrasonic shaking process constitute the theme of the present research work. The fuel properties tested in the study include flash and fire points, viscosity, cloud point, and pour point. In order to obtain the performance and emission characteristics, and thus relate between the engine performance and environmental impact to the dosing level of the fuel additive, performance tests were carried out on a single cylinder water-cooled direct injection diesel engine. The performance and emission characteristics of biodiesel, in the pure form and in the presence of various dosing levels of the nanoparticle additives are presented.

ISSN2321-2152www.ijmece .com
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Experimental Study

The experimental investigations were carried out in two phases. In the first phase, the various physicochemical properties of modified bio diesel were determined and compared with those of the base fuels. The properties studied were the flash and fire points, cloud and pour points and viscosity. Standard ASTM test procedures were used in the experiments. In the second phase, extensive performance 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 nanoparticles of size 10 to

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 theperformance test facility are all presented below.

Preparation of Modified Fuels. The fuel used for the current investigation is a bio diesel product, derived from Jatropha. The viscosity, density, and Calorific value of the bio diesel were measured using standard equipment and are 52 cSt at 32°C, 906 kg/m^3 and 34.5 MJ/Kg, respectively. The fuel additive used in this investigation is cerium oxide, in the form of commercially available

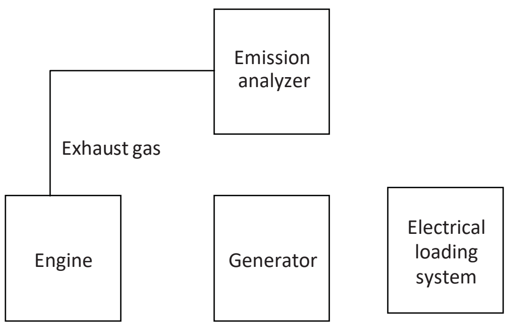
TABlE 1: Engine specifications.

Type	Naturally aspirated, four stroke, single cylinder, water-cooled compression ignition
Stroke	110 mm
Bore	88 mm
Rated output	5.5 kW
Rated speed	1500 RPM
Loading devise	Electrical generator

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 20 to 80 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.

Determination of Fuel Properties. The viscosity, flash and fire points, and the pour and cloud points were measured using standard test methods**.** The viscosity was measured using the Redwood viscometer [19]. A Cleveland open cup flash and fire point apparatus [20] was used for measuring the flash point, and a standard cloud and pour point apparatus was used for measuring the cloud and pour points [21].

Description of the Test Engine. A four stroke, single cylinder, water-cooled compression ignition engine was used to conduct the performance and emission studies. Standard constant speed load tests were also performed on the engine. An electrical generator was used for loading the engine. Specifications of the engine used for the performance study are given in Table 1, and a schematic block diagram of the experimental test facility is illustrated in Figure 1.



Results and Discussion

The ASTM standard tests to determine various physico-chemical properties of the base fuels (Bio diesel) as well as

Dosing level of CeO_2 (ppm)

FIGURE 2: Variation of flash point with nanoparticle dosing level for biodiesel.

ISSN2321-2152www.ijmece .com
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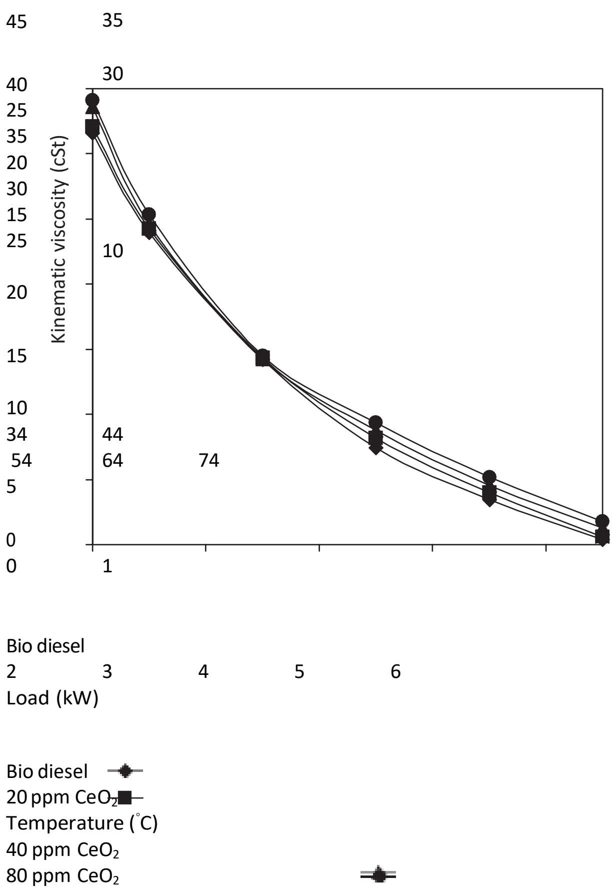
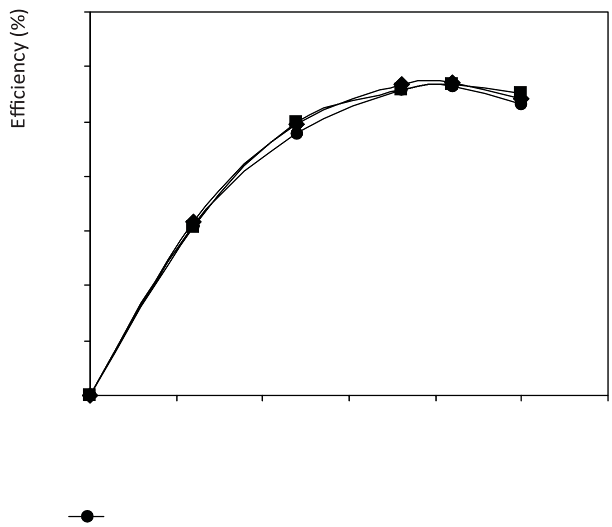
the modified fuels were carried out under identical labora- tory condition so that the results could be compared. The primary objectives of this investigation were to determine the variations in the properties of the fuels, due to the addition of the cerium oxide nanoparticles and to estimate the effect 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.

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 bio diesel as a function of the dosing level. As illustrated, the bio diesel 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 and the temperature on the kinematic viscosity of bio diesel are illustrated in Figure 3, which indicates that the viscosity of the fuel decreases with an increase in the temperature for all dosing levels. Also, it is clear that the maximum percentage variation in the viscosity occurs at the highest temperature. In addition, it is apparent that the nanoparticles added to the fuel increase the fluid layer resistance and hence, increase the viscosity. 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





40 ppm CeO_2
80 ppm CeO_2

Figure 4: Variation of the brake thermal efficiency with load forbio diesel and modified bio diesel with different dosing levels of the
Figure 3: Variation of the kinematic viscosity of biodiesel with temperature at different dosing levels of the additive.

Table 2: Cloud and pour points of biodiesel.

	Cloud point	Pour point
Biodiesel	6°C	□1°C
Modified biodiesel	6°C	□1°C(dosing level 40 ppm)

of fuel injection pumps or injector plungers resulting in leakage or increased wear thus reducing the maximum fueldelivery. This imposes a limitation on the quantity of the fuel additive that can be used in enhancing the combustionperformance 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.

No significant differences were observed in the cloud and pour points due to the addition of catalyst nanoparticles in the bio diesel, as shown in Table 2 summarizing the measurement of these properties. This indicates that the addition of cerium oxide nanoparticles does not have any significant effect on the cold temperature properties of bio diesel, and no strategic difference is required in the cold handling of the modified fuels.

additive.

The cerium oxide nanoparticles present in the fuel promote longer and more complete combustion, compared to the base fuel as cerium oxide acts as an

3.2. Engine Performance. Figure 4 illustrates the results of the performance tests conducted on the diesel engine withstandard bio diesel oil and modified fuel. The results

$$\left(2x + y\right) CeO_2 + C_xH_y \longrightarrow \left(\frac{2x + y}{2}\right) Ce_2O_3 + \frac{x}{2} CO_2 + \frac{y}{2} H_2O. \quad (1)$$

oxygen buffer andthus increases the efficiency. It has also been observed that the improvement in the efficiency generally increases with the dosing level of nanoparticles. A maximum increase of 1.5% in the brake thermal efficiency was obtained when the dosing level was varied from 20 to 80 ppm, with a maximum improvement observed at a dosing level of 80 ppm. Cerium oxide oxidizes the carbon deposits from the engine leading to efficient operation and reduced fuel consumption. Cor- responding to the efficiency characteristics, the specific fuel consumption decreases with an increase in the dosing levelof nanoparticles.

3.3. Emissions. The hydrocarbon emissions have been mea- sured for both the base fuel and the modified fuel using anemission analyzer. Figure 5 shows the variation of hydro- carbon emissions for different dosing levels of the fuel additive in bio diesel. Hydrocarbon emission is found to be significantly reduced on the addition of the additive. Cerium oxide has the ability to undergo a transformation from the stoichiometric CeO_2 (+4) valance state to the Ce_2O_3 (+3) state via a relatively low-energy reaction. Cerium oxide supplies the oxygen for the reduction of the hydrocarbon aswell as the soot and gets converted to cerous oxide (Ce_2O_3)as follows [22].

Hydrocarbon combustion:

show that the brake thermal efficiency of the diesel engine is improved by the addition of cerium oxide in the fuel.

ISSN2321-2152www.ijmece .com
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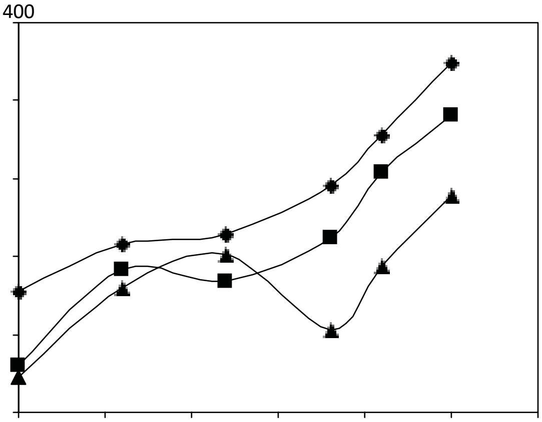
200 400

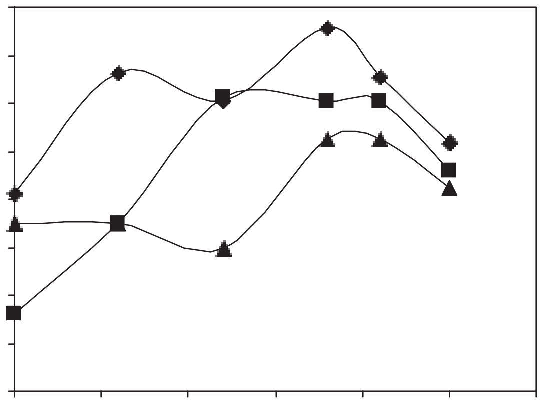


160

120 Hydrocarbon (ppm)

80
350
300
250
200
150

40



NO_x (ppm)

Bio diesel
40 ppm CeO_2
80 ppm CeO_2
3 4 5 6
Load (kW)

Figure 6: Variation of NO_x emissions with load for differentadditive dosing levels in bio diesel.

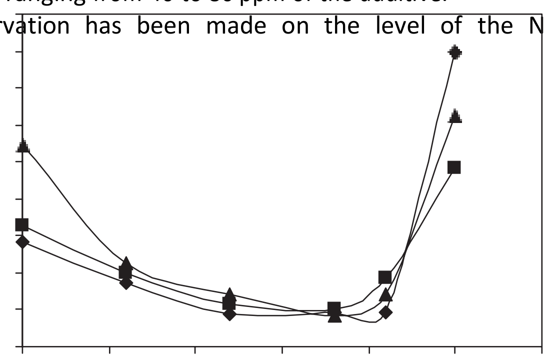
Soot burning:

$4CeO_2 + Csoot \rightarrow 2Ce_2O_3 + CO_2$. (2)

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 25% to 40% in the hydrocarbon emissions was obtained for additive dosing levels ranging from 40 to 80 ppm of the additive.

Observation has been made on the level of the NO_x emissions from bio diesel, in the pure form and in the modified form. Due to its high thermal stability, Ce_2O_3 formed from the oxidation of hydrocarbon and soot remainsactive after enhancing the initial combustion cycle and gets reoxidized to CeO_2 through the reduction of nitrogen oxideas per the following reaction:

0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0



CO (%)

1 2

Bio diesel
40 ppm CeO_2
80 ppm CeO_2
3 4 5 6
Load (kW)

$$Ce_2O_3 + NO \rightarrow 2CeO_2 + \frac{1}{2}N_2. \quad (3)$$

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It is found that the NO_x emission, as expected, is influenced by the addition of the cerium oxide nanoparticles in bio diesel as shown in Figure 6. The NO_x emission was found to be generally reduced on the addition of cerium oxide nanoparticles to bio diesel, as shown in Figure 6, where an average reduction of around 30% was found to occur with a dosing level of 80 ppm nanoparticles. In general, there is a reduction in NO_x emission due to the addition of cerium oxide. A detailed flame analysis could possibly lead to the exact reasons behind the observed phenomenon, as the behavior could be due to a complex interaction among factors such as the combustion temperature, reaction time, and the oxygen content.

Figure 7 shows the influence of a catalyst addition on carbon monoxide emissions. The reduction influence ofFigure

7: Variation of CO emissions with load for different additive dosing levels in bio diesel.

Conclusions

One of the methods to vary the physicochemical properties and combustion characteristics of a hydrocarbon fuel is theuse 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, and emissions. The major observations and inferences are listed below.

The flash point of bio diesel, which is an indicationof the volatility was found to increase with the inclusionof the additive. The viscosity of bio diesel was found to increase with the addition of cerium oxide nanoparticles. The viscosity and the volatility were found to hold direct relations with the dosing level of the nanoparticles, within the rangeanalyzed (20–80 ppm).

The cold temperature properties of bio diesel do not show significant variation, due to the addition of cerium oxide nanoparticles. Engine tests with the modified bio diesel at different dosing levels (20–80 ppm) of the additive showed an improvement in the efficiency of the engine. Emission levels of hydrocarbon and NO_x are appreciably reduced with the addition of cerium oxide nanoparticles. It is understood that cerium oxide being thermally stable promotes the oxidation of hydrocarbon and reduction of nitrogen oxide, thus acting as an effective catalyst, when added in the nanoparticle form.

Experimental work is underway on the effect of parameters such as the preparation time and the nanoparticle size, apart from the dosing level, on the performance of the fuelsmodified with cerium oxide nanoparticles. Efforts are also being made to obtain the optimum combinations of these parameters for the best performance of the fuel. Analysis of the combustion and flame characteristics of the catalystenhanced fuel using visualization techniques is also being undertaken as part of continuing research.

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