Effects of particle size of cerium oxide nanoparticles on the combustion behavior and exhaust emissions of a diesel engine powered by biodiesel/diesel blend

P. Dinesha1, Shiva Kumar1,*, Marc A. Rosen2

1Department of Mechanical and Manufacturing Engineering, Manipal Institute of Technology, Manipal Academy of Higher Education, Manipal-576104, India.
2Faculty of Engineering and Applied Science, University of Ontario Institute of Technology, 2000 Simcoe Street North, Oshawa, Ontario, L1G 0C5, Canada.

GRAPHICAL ABSTRACT

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Meeting the emission norms specified by governing bodies is one of the major challenges faced by engine manufacturers, especially without sacrificing engine performance and fuel economy. Several methods and techniques are being used globally to reduce engine emissions. Even though emissions can be reduced, doing so usually entails a deterioration in performance. To address this problem, nanoadditives such as cerium oxide (CeO2) nanoparticles are used to reduce engine emissions while improving engine performance. However, some aspects of the application of these nanoadditives are still unknown. In light of that, three sizes of CeO2 nanoparticles (i.e., 10, 30, and 80 nm) were compared.

Effects of different sizes of CeO2 nanoparticles on diesel engine combustion was studied. Biodiesel-diesel blend harboring CeO2 nanoparticles of different sizes, i.e., 10, 30, and 80 nm were compared. Fuel consumption dropped by 2.5% for 30 nm nanoparticles-doped fuel blend vs. its additive-free counterpart. Smoke opacity and NOx concentration decreased by 34.7% and 15.7% for fuel formulation harboring 30 nm CeO2 nanoparticles.

ABSTRACT

The results showed that the addition of CeO2 nanoparticles led to performance improvements by reducing brake specific fuel consumption. Moreover, the catalytic action of CeO2 nanoparticles on the hydrocarbons helped achieve effective combustion and reduce the emission of carbon monoxide, unburnt hydrocarbon, oxides of nitrogen, and soot. Interestingly, the size of the nanoadditive played an instrumental role in the improvements achieved, and the use of 30 nm-sized nanoparticles led to the most favorable performance and the lowest engine emissions. More specifically, the fuel formulation harboring 30 nm nanoceria reduced brake specific fuel consumption by 2.5%, NOx emission by 15.7%, and smoke opacity by 34.7%, compared to the additive-free B20. These findings could shed light on the action mechanism of fuel nanoadditives and are expected to pave the way for future research to develop more promising fuel nanoadditives for commercial applications.

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Abbreviations

B20  20% WCO biodiesel and 80% mineral diesel
B20+10nm B20 + 10 nm CeO₂
B20+30nm B20 + 30 nm CeO₂
B20+80nm B20 + 80 nm CeO₂
BSEC Brake specific energy consumption (MJ/kWh)
BTE Brake thermal efficiency (%)
CeO₂ Cerium oxide
CeO₃ Cerous oxide
Dₚ Nanoparticle diameter (nm)
dQᵢ/dθ Instantaneous heat release rate (J/deg CA)
HSU Hartridge smoke unit
Kᵣ Base fluid thermal conductivity (W/mK)
Kₙ Nano fluid thermal conductivity (W/mK)
Kₚ Nanoparticle thermal conductivity (W/mK)
p Pressure (bar)
X₁CO Carbon monoxide concentration (%vol)
X₁CO₂ Carbon dioxide concentration (%vol)
Xᵣ Hydrocarbons concentration (ppm)
XₙOₓ Oxides of nitrogen concentration (ppm)
WCO Waste cooking oil
T Temperature (°C)
V Volume (m³)
γ Ratio of specific heats
ε Volume fraction of nanoparticles (%)

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1. Introduction

Diesel fueled engines are commonly used prime movers in the transport and industrial sectors, partly because they have high thermal efficiencies and good reliability. Dependence on diesel engines has increased, leading to elevated fossil fuel consumption. On the other hand, the largest sources of greenhouse gas emissions are prime movers that use conventional fuels such as diesel (Agarwal, 2007). Substituting fossil fuels with renewable options such as biofuels can help reduce carbon emissions (Kumar and Dinesha, 2019).

Vegetable oil and animal fat serve as raw materials for the manufacturing of biodiesel. Transesterification redefines the molecular structure of the materials involved in producing biodiesel, rendering it suitable as an alternative for diesel engines (Rakopoulos et al., 2006; Sureshkumar et al., 2008; Muralidharan et al., 2011). Neat biodiesel suffers certain shortcomings like increased NOx, low energy output, and high specific fuel consumption (An et al., 2013). The usage of additives has been shown to be able to overcome these limitations by meeting specific fuel requirements (Agarwal et al., 2008; Alptekin, 2017; Dinesha et al., 2019). Marginal reductions in emissions are observed when using microscale sized additives, but studies indicate that the usage of large additive particles could adversely affect combustion performance, leading to increases in emissions and decreases in efficiency (Bertola et al., 2003; Qi et al., 2009; Izquierdo et al., 2012). This phenomenon could be explained by the higher density of the additive-containing droplets, making it difficult to have a uniform mixture of fuel and additives. This could also result in the settling of the additive-containing droplets, leading to sedimentation. Another disadvantage is that when larger particles are injected along with the base fuel, they take more time to complete physical and chemical processes, resulting in higher ignition delay. A higher delay period leads to incomplete combustion and increased exhaust emissions. Hence, these factors limit the use of large-sized additives in biodiesel blends.

Nevertheless, these limitations can be overcome by applying nano-sized metal or metal oxide particles (<100 nm) in biodiesel blends. They have specific advantages such as higher surface to volume ratio, higher thermal conductivity, and better lubricating properties than micro-sized additives (Kumar et al., 2018; Kumar et al., 2019a). When nanoparticles are mixed with a base fluid such as water, diesel, biodiesel, etc., the resulting mixture is known as a nanofluid. Compared to the base fluid, the nanofluid has distinct advantages like higher thermal conductivity and improved lubricity. These properties help with the efficient transfer of heat, which is essential during engine combustion. Furthermore, relatively small diameters of nanoparticles reduce sedimentation by enhancing their dispersion and also increasing chaotic movements. When a nanofluid is injected through the fuel injector into the combustion chamber, an increase in heat exchange between biodiesel and air could be achieved due to the nanofluid's higher thermal conductivity mentioned earlier. This quickly prepares the air-fuel mixture to undergo spontaneous combustion compared to neat fuel combustion, reducing ignition delay. Hence, enhanced combustion and engine performance can be achieved with lower emissions.

For over a decade, researchers have been investigating the effects of nanosized additives in diesel engines (Rao and Dash, 2015) studied the role of particle size on the spreading stability of aluminum nanoparticles (13 nm and 28 nm in size) after their addition to Jatropha-based biodiesel. They reported that the 13 nm nanoparticles with a 0.1% volume fraction were stable for more than one year. Kumar et al. (2017) investigated the influence of ferric nanoparticles on the performance and emissions characteristics of a diesel engine powered by biodiesel. By adding 1% (v/v) of ferrofluid nanoadditive to B20, the authors observed a higher brake thermal efficiency (BTE), lower fuel consumption, and lower concentrations of carbon monoxide (X₁CO) and hydrocarbon (X₁HC). Prabu (2018) experimentally studied the operational characteristics of a conventional diesel-fueled engine with alumina (Al₂O₃) and ceria (CeO₂) nanoparticles. They reported that Al₂O₃ as a nanoadditive yielded a higher BTE than the nanoceria and that the presence of nanoparticles, in general, diminished the delay and accelerated early initiation of combustion.

Ramesh et al. (2018) investigated the effects of adding alumina-based nanoparticles into poultry litter-based biodiesel on the performance, emissions, and combustion behavior of a diesel engine. They reported that biodiesel with alumina nanoparticles exhibited a better BTE than neat biodiesel fuel. D'Silva et al. (2019) studied the effects of titanium dioxide nanoparticles (25, 50, and 75 ppm) inclusion in Pongamia biodiesel (B20).
on diesel engine combustion. More efficient fuel combustion was noticed for the nanoparticle-blended fuels with considerably reduced emissions, except for nitrogen oxides (NOx). The authors highlighted that the fuel blend harboring 75 ppm nanoparticles exhibited the most promising results. Kao et al. (2007) performed combustion experiments on a diesel engine using fuels containing an aqueous aluminum nanofluid. They observed an improvement in burning rate in the presence of the aqueous aluminum nanofluid. Similarly, Xin et al. (2013) argued that the addition of nanoceria as nanoadditives improved the combustion efficiency, likely due to the elevated pressure and extension in burning duration.

It has also been reported that nanoparticle-blended fuels were associated with shorter ignition delays vs. conventional diesel fuel and that the maximum achievable cylinder pressure of fuel blends with nanoparticles was more significant than that for neat conventional diesel (Kumar et al., 2019a). Kumar et al. (2019b) tested the combined impact of injection pressure (180, 210, and 240 bar) and nanoceria (80 ppm) on the thermal behavior of a diesel engine running on biodiesel (B20). Better performance with lower emissions was observed for the cerium oxide nanoparticle-doped fuel at the highest injection pressure of 240 bar.

Sajith et al. (2010) also experimentally explored the impact of nanoceria as a fuel additive in Jatropha biodiesel. They reported that, at full load, the BTE using nanoparticle-dispersed biofuel was higher than that using neat biodiesel. Also, the CeO2 nanoparticle-doped fuel formulation exhibited lower NOx concentrations (XNOx). Similarly, Mirzajanzadeh et al. (2015) also argued that the combustion of cerium oxide nanoparticle-blended fuel (diesel/waste cooking oil (WCO) biodiesel/CeO2 (40-50 nm) nanoparticles) led to considerable mitigation of NOx emissions. The authors used different concentrations of the nanoadditive, i.e., 30, 60, and 90 ppm, and recorded the maximum reduction in XNOx of 18.9% for the highest CeO2 nanoparticles concentration of 90 ppm. Selvan et al. (2009) also claimed a 54% reduction in XNOx when the investigated diesel engine was operated with fuel formulations harboring CeO2 nanoparticles. Table 1 summarizes the results reported by the latest studies on the performance and emission characteristics of diesel engines powered by diesel/biodiesel blends carrying nanoceria as a fuel additive.

The performance of an engine operating with diesel and biodiesel fuel blends containing nanoadditives could be strongly influenced by biodiesel type and the different features of the nanoparticles used as an additive (type, size, morphology, oxide layer thickness, and volume fraction). The effects of various biodiesel types and variations in nanoparticle volume concentrations have been widely investigated. However, little is known about the impact of nanoparticle size on engine performance and emission characteristics. In light of that, this work aims to bridge this knowledge gap by investigating the performance and emission characteristics of a diesel engine powered with a biodiesel/diesel fuel blend (B20; WCO biodiesel) harboring CeO2 nanoparticles of varying sizes (10, 30, and 80 nm). Performance parameters (including brake specific energy consumption (BSEC), peak cylinder pressure, and heat release rate) and engine tailpipe gas emissions (including XCO, XH2, XNOx, and smoke opacity) were measured and analyzed.

2. Background: role of CeO2 nanoparticle catalyst in engine combustion

Ceria is a naturally occurring rare earth element with two valence states, +3 and +4. Ceria in +4 state is a non-trivalent rare-earth ion and a potent oxidizing agent. Ceria in +3 state resembles other trivalent rare earth elements. Ceria is widely used in the form of CeO2. It is a highly stable, non-toxic refractory material that melts at 2600 °C and has a density of 7.13 g/cm3. It adopts the fluorite crystal structure with space group Fm3m, #225 containing 8-coordinate Ce4+ and 4-coordinate O2-. The face-centered cubic (FCC) structure of stoichiometric cerium oxide, with four coordinated oxygen anions represented by large red balls and eight coordinated cerium cations represented by small blue balls, is shown in Figure 1 (Malavasi et al., 2010).

At high temperatures, cerium oxide discharges oxygen to provide an anion deficient form that maintains the fluorite lattice. Cerium oxide is widely used in catalysis, polishing, optics, mixed conduction, fuel cells, and engine applications (Mehrizi et al., 2018). Since the transformation from a +4 valence state to a +3 valence state is a low energy reaction, CeO2 is widely used as a catalyst in combustion reactions. Oxygen storage tendency of CeO2 during the catalysis process is shown in Equation 1 (Kaspar et al., 2000):

\[2\text{CeO}_2 \rightarrow \text{Ce}_2\text{O}_3 + 0.5_2 \]

When CeO2 nanoparticles are added to a hydrocarbon-based fuel such as diesel and biodiesel, the inherent properties of CeO2 help reduce the hydrocarbon content and oxidize the soot particles, according to Equations 2 and 3, respectively.

\[(2x + y)\text{CeO}_2 + x\text{H}_2 \rightarrow \left[\frac{(2x+y)}{2}\text{Ce}_2\text{O}_3 + \frac{y}{2}\text{CO}_2 + \frac{y}{2}\text{H}_2\text{O}\right] \]

\[4\text{CeO}_2 + x\text{CeO}_2 \rightarrow 2\text{Ce}_2\text{O}_3 + \text{CO}_2 \]

CeO2 has a tendency to reduce NOx emissions. Initially, it reacts with hydrocarbons, forming cerous oxide (Ce2O3). When Ce2O3 combines with oxides of nitrogen, the oxidation reaction takes place and it is re-oxidized to CeO2. The formation of nitrogen from NOx is presented in Equation 4.

\[\text{Ce}_2\text{O}_3 + \text{NO} \rightarrow 2\text{Ce}_2\text{O}_3 + \frac{y}{2}\text{N}_2 \]

In addition to the catalytic property of CeO2, another significant advantage of this compound is its outstanding thermal conductivity making it suitable for use in heat transfer applications. The heat transmission rate of the nanoparticles directly relates to the conductivity of the nanofluid.

| Table 1. Main Summary of the findings of the latest studies on the application of nanoceria in various diesel/biodiesel blends. |
| Fuel formulation | Main results | Ref. |
|-------------------|--------------|------|
| Neem oil biodiesel + diethyl ether + CeO2 nanoparticles | Combination of B10+150 ppm nanoaditive led to improved BTE with decreased emissions | Kapoor et al. (2020) |
| Lemongrass biofuel + 30 ppm CeO2 : | BTE was increased by 17.2% with lower engine emissions for the fuel formulation harboring nanoparticles | Venkatesan et al. (2019) |
| Algae biodiesel + 25, 50, 75, and 100 ppm CeO2 : | B20 with 100 ppm nanoparticles showed maximum BTE | Kalaimurugan et al. (2020) |
| Biodiesel + 50, 100, and 150 ppm of CeO2 : | Improved performance and reduced emissions for B20 +150 ppm nanoceria | Kumar et al. (2020) |
| WCO biodiesel + Fe-doped CeO2 : | Peak cylinder pressure was increased by 3.5%, and XNOx was reduced by 7% for B30 doped with FeCeO nanoparticles | Haiw et al. (2019) |
| Waste coookinh oil (WCO) biodiesel + CeO2 nanoparticles + cerium composite oxide | Fuel blend containing CeO2 nanoparticles + cerium composite oxide led to lower engine emissions with better performance | Akram et al. (2019) |
| Pomagia biodiesel + CeO2 and CeO2 Gd | Reduced XuO and smoke opacity were obtained for biodiesel harboring CeO2-Gd nanoparticles | Dhanasekar et al. (2019) |
| Cinnamom oil + diesel + CeO2 nanoparticles | Reduced XNOx and XuO emissions were obtained for B30 containing 300 ppm CeO2 nanoparticles | Senthil Kumar et al. (2019) |
| Mahua biodiesel + 50 and 100 ppm CeO2 | BTE was increased by 1.8%, while XNOx and XuO were reduced for B20 doped with 100 ppm CeO2 nanoparticles | Seela et al. (2019) |

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When the nanoparticles are distributed in a base fluid such as biodiesel, the effective heat conductivity is enhanced. Furthermore, the size of the nanoparticles has a strong influence on the thermal conductivity of the nanofluid. Assuming CeO$_2$ nanoparticles to be spherical in shape, the ratio of thermal conductivity of the nanofluid to the base fluid (neat B20) can be calculated using Equation 5 (Patel et al., 2010):

$$\frac{K_{nf}}{K_f} = \left[ 1 + 0.135 \times \left( \frac{D_p}{\nu_f} \right)^{0.273} \times e^{0.467 \times \left( \frac{T}{100} \right)^{0.547} \times \left( \frac{\rho_f}{\rho_p} \right)^{0.234}} \right] \quad \text{Eq. 5}$$

where, $K_{nf}$, $K_f$, and $K_p$ are the thermal conductivities (W/mK) of the nanofluid, the base fluid, and the nanoparticles, respectively. $\varepsilon$ is the volume fraction of the nanoparticle (%), $T$ stands for the operating temperature (°C), and $D_p$ denotes the nanoparticle size (nm).

Equation 5 takes into account the size of the particle, its volume concentration, and temperature. Figure 2 depicts changes in the thermal conductivity of a nanofluid vs. changes in the volume fraction of several sizes of nanoparticles, as calculated using Equation 5. It is observed that $K_{nf}$ increases as the volume fraction is increased. Also, when the particle size is increased, $K_{nf}$ decreases. The increase in the specific surface area and enhanced Brownian motion of the particles might be the reasons to the higher $K_{nf}$ for smaller particle sizes. A smaller size particle has a more excellent surface-to-volume ratio, which in turn augments heat transfer to the base fluid. In addition, a small particle possesses higher Brownian motion velocity, which causes the heat transfer to occur at a faster rate. All these effects contribute to increasing the effective thermal conductivity and, correspondingly, to the heat transfer rate of the nanofluid (Iyahraja and Rajadurai, 2015).

### 3. Materials and Methods

#### 3.1. Fuel blend preparation

Esterified WCO biodiesel was procured from a local supplier. The physiochemical properties of neat WCO biodiesel complied with the American Society for Testing and Materials (ASTM) standard and those of B20 (20% biodiesel and 80% diesel) and listed in Table 2. Three sizes of cerium oxide nanoparticle (viz. 10, 30, and 80 nm) were used to prepare the test fuels. The concentration of the nanoparticles was kept constant at 80 ppm. The fuel formulations were designated as B20+10nm, B20+30nm, and B20+80nm. A suitable surfactant was selected and used in the present work to have a uniform dispersion of cerium oxide nanoparticles in investigated fuel blends. The choice of a surfactant would depend on the hydrophilic-lipophilic balance (HLB) of the surfactant, and in this case, it had to be soluble in the B20. Having screened various surfactants, dodecylsucinonic anhydride (DDSA-C$_{16}$H$_{34}$O$_3$), having a HLB value of 1.34 (Sajeevan and Sajith, 2013), was selected. The test fuel blends were processed by ultra-sonification for 0.5 h until CeO$_2$ nanoparticles were well distributed in the fuel blends.

#### 3.2. Test setup and experimentation

The experiments were conducted on a Kirloskar TY1 four-stroke engine. It consisted of a single-cylinder with a water-cooled facility. Specifications of the engine are shown in Table 3. Figure 3 depicts a schematic presentation of the engine setup used in the present study. An eddy current type dynamometer was used for loading, and sensors are attached to determine temperatures. The cooling water flow rate of the engine jacket was measured using a rotameter. A computer connected to the setup generated pressure vs. crank angle plots from the signals. Fuel flow measurement was taken using a burette. An AVL exhaust gas analyzer and an AVL smoke meter were used to quantify emissions data. The range and resolution of the instruments used in the experiments are provided in Table 4.

#### Table 2. Physicochemical properties of B20 WCO biodiesel.

| Property                      | Value |
|-------------------------------|-------|
| Flash point (°C)              | 66    |
| Fire point (°C)               | 73    |
| Calorific value (MJ/kg)       | 40.3  |
| Kinematic viscosity (cSt)     | 3.7   |
| Density (kg/m$^3$)            | 843   |

#### Table 3. Specifications of diesel engine.

| Specification                  | Value/description |
|-------------------------------|-------------------|
| Bore diameter (mm)            | 87.5              |
| Stroke length (mm)            | 110               |
| Compression ratio             | 17.5:1            |
| Rated brake power (kW)        | 5.2 at a constant speed of 1500 rpm |
| Normal Injection pressure (bar)| 180               |
| Swept volume (cm$^3$)         | 661               |

#### Table 4. Range and resolution of the instruments.

| Item                           | Range     | Resolution |
|-------------------------------|-----------|------------|
| Pressure (bar)                | 0.344 – 75| 0.0069     |
| Smoke opacity                 | 0 – 100   | 0.01       |
| NOx concentration (ppm)       | 0 – 5000  | 1          |
| CO concentration (vol)        | 0 – 10%   | 0.01%      |
| HC concentration (ppm)        | 0 – 20,000| 10         |
| CO concentration (vol)        | 0 – 20%   | 0.1%       |

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3.3. Heat release rate

The instantaneous rate of heat release during burning was determined by Equation 6 (Heywood, 2018).

\[
\frac{dQ}{d\theta} = \frac{\gamma}{\gamma - 1} p \frac{dV}{d\theta} + \frac{1}{\gamma - 1} V \frac{dp}{d\theta}
\]

where \(\frac{dQ}{d\theta}\) denotes instantaneous heat release rate per degree crank angle (J/degree), \(\gamma\) ratio of specific heats, \(p\) cylinder pressure (bar), \(V\) cylinder volume (m\(^3\)), and \(\theta\) crank angle in degree, while \(\frac{dV}{d\theta}\) and \(\frac{dp}{d\theta}\) stand for instantaneous change in the cylinder volume and pressure per degree crank angle, respectively.

3.4. Uncertainty analysis

In laboratory experiments, uncertainty analysis deals with evaluating the uncertainty in any measurements. It allows estimation of the numerical value of a physical variable and how it is affected by errors due to instrumentation. In the present work, the uncertainty of a dependent variable was calculated using errors involved in measuring independent parameters such as load, speed, and fuel flow rate, using Equation 7.

\[
W_R = \left( \frac{\partial R}{\partial x_1} W_1 \right)^2 + \left( \frac{\partial R}{\partial x_2} W_2 \right)^2 + \cdots + \left( \frac{\partial R}{\partial x_n} W_n \right)^2 \right)^{1/2}
\]

The calculated uncertainty values for various parameters are listed in Table 5.

Table 5.
Uncertainty analysis of selected measured parameters used in the study.

| Measured quantity               | Percentage uncertainty |
|---------------------------------|------------------------|
| Load                            | 0.65                   |
| Speed                           | 0.51                   |
| Fuel flow rate                  | 0.8                    |
| Brake specific fuel consumption | 1.4                    |
| \(X_{CO}\)                      | 2.0                    |
| \(X_{HC}\)                      | 2.1                    |
| \(X_{CO}\)                      | 1.4                    |
| Smoke opacity                   | 0.65                   |

4. Results and Discussion

Test trials were conducted for several sizes of cerium oxide nanoparticles with a constant volume fraction of 80 ppm. Engine performance parameters, i.e., BSEC, peak cylinder pressure, and heat release rate, and tailpipe emissions, i.e., \(X_{NOx}, X_{CO}, X_{HC}\), and smoke opacity for the investigated fuel formulations (B20+10nm, B20+30nm, and B20+80nm) and neat B20 as baseline are presented in the following subsections.

4.1. CeO\(_2\) nanoparticles as a combustion promoter

4.1.1. Cylinder peak pressure and heat release rate

Cylinder peak pressure is an indication of combustion efficiency. If the fuel mixture undergoes complete combustion in the premixed phase, a higher cylinder pressure can usually be attained. This also results in increased power output with reduced emissions. From the data depicted in Figure 4, it can be observed that the cylinder peak pressure obtained with CeO\(_2\) nanoparticles-doped fuels was greater than that of additive-free B20. When CeO\(_2\) nanoparticles were added to the B20 fuel blend, they must have acted as heat carrier media, promoting heat flow among the fuel droplets and air. This phenomenon must have caused faster vaporization of the fuel droplets, reducing the delay period. Therefore, the autoignition temperature was attained faster relative to additive-free B20. These factors contributed to smooth combustion and the attainment of a higher cylinder peak pressure close to the top dead center (TDC). Among the different fuel formulations, the one containing 30 nm nanoparticles exhibited a higher peak pressure than the other two. When the particle size increases, the surface-to-volume ratio decreases, resulting in reduced heat transfer, as seen in the case of B20+80nm. This fuel formulation exhibited the lowest value of peak cylinder pressure among the three fuel variants (Fig. 4).

Figure 5 shows the net heat liberation rate for the fuels tested at full load conditions. The heat liberation rate is a function of the rate of pressure rise. However, it should also be noted that when the particle size is too small, despite the higher surface-to-volume ratio, the transport characteristics of the fuel particles decrease due to reduced density. This in turn could result in poor mixing of the air and fuel as a local stoichiometric mixture. Also, the agglomeration tendency would be higher for too small particles. Hence, for the B20+10nm fuel blend, the peak pressure attained was moderate, whereas it was the largest for the B20+30nm fuel blend. Therefore, nanoparticle size of 30 nm could be regarded as optimum, exhibiting better combustion characteristics compared to the other nanoparticle sizes tested.

Figure 5 shows the net heat liberation rate for the fuels tested at full load conditions. The heat liberation rate is a function of the rate of pressure rise.
in the cylinder, as shown in Equation 6. Generally, when the peak cylinder pressure is higher, the rate of pressure rise is considerably higher. The higher rate of pressure rise is possible due to the better combustion achieved during the initial phase of combustion (i.e., premixed phase). The combined influence of a superior heat transfer mechanism and the catalytic action of \( \text{CeO}_2 \) nanoparticles must have played a major role in achieving a more significant cylinder pressure rise and hence, a greater heat release rate (Fig. 5). The catalytic action of \( \text{CeO}_2 \) oxidizes any unburnt hydrocarbon (UHC) and carbon monoxide present to \( \text{CO}_2 \), liberating energy. This accounts for the total heat released during combustion. Compared to the baseline B20, the nanoparticles-doped fuel formulations exhibited greater heat release rates, with B20+30nm ranked as the highest. The reasons for these observations could be the better fluid transport and thermal characteristics of 30 nm-sized nanoparticles, as previously discussed on the cylinder peak pressure.

The cumulative heat release is dependent on several factors such as the start and end of combustion, fuel nature and quality, and rate of pressure rise in the cylinder. The presence of \( \text{CeO}_2 \) nanoparticles acted as a combustion promoter leading to the conversion of CO and UHC to \( \text{CO}_2 \) by catalytic oxidation. This resulted in the release of additional energy, which would have been otherwise left as unburnt fuel in the exhaust. This additional energy increased the cumulative heat release during combustion, increasing the power output correspondingly. A comparison of the three test fuel formulations in Figure 6 indicates that B20+30nm had the highest cumulative heat release.

4.1.2. Brake specific fuel consumption

In general, brake specific fuel consumption (BSEC) represents the energy consumption per unit specific engine output (brake power). BSEC is higher at part load operation and gradually decreases as the load is increased until reaching a minimum at 70-80% of the full of the engine (Mathur and Sharma, 2011). From the data presented in Figure 7, it can be seen that the BSEC for all nanoparticles-doped fuel formulations was lower than for additive-free B20. When \( \text{CeO}_2 \) nanoparticles were doped to the biodiesel blend, a better quality of fuel preparation took place, leading to a more favorable heat flow among the air and fuel droplets. This must have helped with decreasing the ignition delay and improved combustion. These factors likely contributed to reducing BSEC by the effective utilization of the injected fuel. These results are consistent with those reported in the literature previously. For instance, Hawi et al. (2019) observed a lower BSFC for B30 containing iron-doped \( \text{CeO}_2 \) nanoparticles for low to medium loads. At high loads, BSFC was comparable to the results for diesel fuel. Also, Mirzajanzadeh et al. (2015) reported a 4.5% reduction of BSEC for B20 harboring 90 ppm of carbon nanotubes and \( \text{CeO}_2 \) nanoparticles, compared to the corresponding values recorded for the additive-free fuel blend.

Based on the results of the present study, particle size seems to exert a significant effect on fuel consumption. Among the investigated fuel formulation, B20+30nm and B20+80nm were at the extremes, with the former exhibiting minimum BSEC and the latter the maximum. It could be concluded that, in general, BSEC decreased as the nanoparticle size was reduced. As discussed earlier, the surface-to-volume ratio increases for smaller particle sizes, assisting with achieving uniformity in air-fuel mixing. This enhances the heat transfer rate, reducing ignition delay. Reduced ignition delay improves combustion, reducing BSEC. In the present study, the lowest BSEC was observed for an optimum nanoparticle
size of 30 nm. However, when the nanoparticle size was too small, the nanoparticle might not have traversed effectively to various regions in the combustion chamber due to lower density, resulting in non-uniform mixing. This might have increased the ignition delay, leading to poor combustion and consequently a slightly higher BSEC.

4.2. Catalytic action of CeO$_2$ and emission control

Three essential properties are needed for a catalyst for being efficient in diesel engine combustion: (i) completing hydrocarbon oxidation, (ii) preventing the formation of oxides of nitrogen, and (iii) possessing high thermal stability. CeO$_2$ can donate oxygen for the oxidation of hydrocarbons and soot. A unique feature of a CeO$_2$ catalyst is that it activates at low temperature, generally 300-500 °C, and can donate O$_2$ for the oxidation reaction. In diesel engines, combustion takes place at high temperatures, the diesel flame front usually having a temperature of 1700 °C. At this elevated temperature, the formation of oxides of nitrogen during the chemical reactions between nitrogen and oxygen is likely. The CeO$_2$ nanoparticles acted as a catalyst and promoted a more complete burning of the injected fuel. During the reduction of NO to N$_2$, the average cylinder temperature reduces from approximately 1700 °C due to the high activation energy of nitrogen. This further helps to prevent the formation of oxides of nitrogen. In addition, the high thermal stability of CeO$_2$ nanoparticles favors its catalytic activity. Once the initial combustion is achieved, CeO$_2$ undergoes initial oxidation. This is because nanoceria is thermally stable and remains active after re-oxidation for further catalytic action. Hence, CeO$_2$ nanoparticles undergo oxidation and reduction reactions, lowering the X$_{CO}$, X$_{HC}$, and X$_{SO}$ and soot concentration as shown in Equations 2-4.

The catalytic activity of CeO$_2$ is a strong function of its surface area. It has been observed that when the surface area of CeO$_2$ nanoparticle increased by a factor of 20, the carbon combustion activation temperature decreased from 700 to 300 °C (Logothetid is et al., 2003). A higher surface area is obtained by reducing the nanoparticle size. Soot particles and UHC sticking to the combustion chamber walls are oxidized to CO$_2$ when they come into contact, resulting in reduced tailpipe emissions and improved fuel economy. Hence better catalytic action is favored by small CeO$_2$ nanoparticles.

4.2.1. Hydrocarbon, carbon monoxide, and soot oxidation

Figure 8 depicts the variations of X$_{HC}$ for the different fuel formulations at various engine load conditions. As the load increased, the X$_{HC}$ also increased and higher values were observed at full load. HC emissions were lowest at partial load conditions and increased rapidly during the full load operation. The X$_{HC}$ for additive-free B20 fuel was found to be the highest of all fuel blends. This can be attributed to the higher viscosity, reduced penetration, and dispersion leading to poor combustion. When nanoparticles were included, because of the catalytic action of CeO$_2$ according to Equations 1-3, nanoceria could undergo a conversion from a stoichiometric CeO$_2$($^{(+4)}$) valence state to CeO$_2$($^{(+3)}$) state, through a comparatively low energy reaction. This means that cerium oxide gave oxygen for reducing UHC and was thereby converted to cerous oxide, CO$_2$, and water (Meng et al., 2015). When diesel fuel was mixed with CeO$_2$ nanoparticles, the X$_{HC}$ was reduced by 7% compared to neat diesel, similar to the result previously reported by Shaisundaram et al. (2020). Among the different particle sizes examined, B20+30nm exhibited the lowest X$_{HC}$. Even though the surface area provided by 10 nm-sized nanoparticles was higher, the agglomeration and the poor transport capability of the nanoparticles must have led to poor dispersion. This prevented the nanoparticles from reaching the regions where CO and HC formation taking place, resulting in poor combustion and a slight increase in X$_{HC}$. Based on the results of the present study, B20+30nm fuel formulation was associated with the most significant X$_{HC}$ decline of 35% compared to the additive-free B20.

The main reason for CO formation is the shortage of oxygen for the oxidation reaction. When the carbon activation temperature is high, as in the typical diesel engine combustion, the complete transformation of CO to CO$_2$ is complex. At the same time, it takes longer for the conversion process as the activation temperature is higher. CeO$_2$, when added to the fuel, acts as a catalyst and reduces the carbon activation temperature. Hence, the oxidation of CO to CO$_2$ can occur at low temperatures. Due to this phenomenon, a more complete conversion of CO to CO$_2$ could take place, leading to reduced X$_{CO}$. Of the three nanoparticles-doped fuel formulations, B20+30nm exhibits the lowest X$_{CO}$ value, whereas B20+80nm showed the highest, as shown in Figure 9. Nevertheless, these values were respectively 135% and 81% lower than the corresponding value recorded for additive-free B20 operation.

Smoke is comprised of unburnt carbon particles generated during the initial stage of combustion. The main reasons for soot formation are oxygen deficiency and the quenching action occurring near the cylinder wall. Quenching results in the deposition of carbon particles at the wall surface, acting as a barrier for heat transfer. This increases frictional losses, reduces the power output, and consequently, increases fuel consumption. The addition of CeO$_2$ nanoparticles plays a major catalytic role in decreasing soot formation. The carbon activation temperature drops due to the addition of CeO$_2$ to around 200-500 °C. This temperature is sufficient for the oxidation of soot particles to CO$_2$, as shown in Equation 3. Hence, CeO$_2$ reduces the formation of smoke and its emission. Appavu and Venkata Ramanan (2020) also reported reduced smoke opacity for 50 and 100 ppm CeO$_2$ nanoparticle concentrations with Pongamia biodiesel. Seela et al. (2019) observed decreased smoke opacity by 8% when the CeO$_2$ nanoparticles dosage was increased from 50 to 100 ppm. In the present study, of the three nanoparticle sizes considered, the fuel formulation harboring 30 nm-nanoparticles, i.e., B20+30nm, had the lowest soot emission (Fig. 10). The observed value was 53% less than the value measured for the additive-free B20 fuel operation.

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biodiesel combustion, fuel-borne oxygen promotes the oxidation of N\textsubscript{2} to NOx during combustion of biodiesel. NOx formation occurs due to excess oxygen, high combustion temperature, and the relatively long residence time. During biodiesel combustion, fuel-borne oxygen promotes the oxidation of N\textsubscript{2} to NOx, further enhanced by the higher combustion temperature prevailing in the combustion chamber. Several techniques are used to reduce NOx emissions of a diesel engine powered by biodiesel/diesel blend. Biofuel Research Journal 30 (2021) 1374-1383. DOI: 10.18331/BRJ2021.8.2.3

4.2.2. Oxides of nitrogen

The emission of oxides of nitrogen is a major drawback of biodiesel when used in diesel engines. NOx formation occurs due to excess oxygen, high combustion temperature, and the relatively long residence time. During biodiesel combustion, fuel-borne oxygen promotes the oxidation of N\textsubscript{2} to NOx, further enhanced by the higher combustion temperature prevailing in the combustion chamber. Several techniques are used to reduce X\textsubscript{NOx} in the tailpipe exhaust (Brijesh and Sreedhara, 2013). Although they reduce X\textsubscript{NOx}, these techniques also increase the X\textsubscript{HC} and X\textsubscript{CO} or reduce the engine performance.

The use of CeO\textsubscript{2} as a catalyst in engines is a novel technique to reduce X\textsubscript{NOx}, simultaneously reducing other emissions without compromising engine performance or even slightly improving it. The catalytic activity of CeO\textsubscript{2} on X\textsubscript{NOx} reduction can be explained by Equation 4, wherein CeO\textsubscript{2} initially undergoes a reaction and forms CeO\textsubscript{3}. This is further reduced to CeO\textsubscript{2} by combining with oxides of nitrogen, liberating nitrogen. During this process, CeO\textsubscript{2} nanoparticles also help reduce the combustion temperature of the fuel-air mixture, as the activation energy of N\textsubscript{2} is higher. Appavu and Venkata Ramanan (2020) also investigated diesel engine performance using Pongamia biodiesel with CeO\textsubscript{2} nanoparticles. The authors observed reduced values of X\textsubscript{NOx} for CeO\textsubscript{2}-doped esters at all loads.

![Figure 10](image1.png)

**Fig. 10.** Variations of smoke opacity for the different fuel formulations against engine load.

From the data presented in Figure 11, it can be observed that the combustion of the additive-free B20 led to the highest X\textsubscript{NOx} under all loading conditions. Among the fuel formulations harboring nanoparticles, B20+30nm exhibited the lowest X\textsubscript{NOx} value, which was 7% less than the corresponding values recorded for B20+10 and B20+80nm.

![Figure 11](image2.png)

**Fig. 11.** Variations for X\textsubscript{NOx} for the different fuel formulations against engine load.

5. Conclusions and future research directions

Experiments were conducted to investigate the performance and emissions characteristics of different B20-based fuel formulations harboring different sizes of CeO\textsubscript{2} nanoparticles. Additive-free B20 was used as control. Based on the results obtained, the following conclusions could be drawn:

- CeO\textsubscript{2} as a catalyst plays a major role in improving engine combustion, increasing BTE and reducing BSFC. The size of the nanoparticles had an instrumental effect on the variations recorded. The 30 nm-sized nanoparticles led to the most significant decrease in BSEC, by 6.4% compared to the additive-free B20.
- The results revealed that the maximum values of heat release rate and cylinder peak pressure were also associated with the B20+30nm fuel formulation.
- The catalytic action of CeO\textsubscript{2} reduced the carbon activation temperature, which helped oxidize the HC, CO, and soot present in the combustion chamber and the quenching regions to carbon dioxide, decreasing engine tailpipe emissions. Furthermore, the B20+30nm fuel formulation resulted in the lowest emissions than the other fuel formulations harboring nanoparticles of smaller or larger sizes. This finding further signified the importance of the size of the fuel nanoadsitives.
- CeO\textsubscript{2} contributed to oxides of nitrogen undergoing oxidation-reduction reactions and hence, to their conversion to nitrogen, keeping X\textsubscript{NOx} at a relatively low value. Again, 30 nm-sized nanoceria was found the most effective in decreasing X\textsubscript{NOx} compared with its 10 nm and 80 nm-sized counterparts.

In general, it can be concluded that the addition of CeO\textsubscript{2} effectively reduced engine emissions while simultaneously improving engine performance. In addition, the nanoparticle size determined the level of the catalytic action of CeO\textsubscript{2} in engine combustion and emission control. These findings highlight the need for further works in this area. Those include but are not limited to optimizing fuel injection characteristics with nanoparticle additives for better engine performance and investigating the effects of two or more nanoparticles and size variations on engine combustion parameters. Moreover, sustainability analysis of various fuel formulations harboring nanoadsitives of different sizes using advanced sustainability assessment tools such as life cycle assessment, exergy, and their combinations should be considered.

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P. Dinesha is an Associate Professor in the Department of Mechanical and Manufacturing Engineering at Manipal Institute of Technology, Manipal Academy of Higher Education (MAHE), Manipal, India. MAHE is an outstanding private university having “Institute of Eminence” status declared by the Ministry of Human Resource Development, Government of India. Dr. Dinesha has obtained a doctoral degree from the National Institute of Technology Karnataka (NITK), Surathkal, India, in the area of alternative fuels. NITK is a preeminent institution of national importance established by the Indian Parliament and is consistently ranked within the top ten technical institutions in India. Dr. Dinesha has published more than 50 research papers in national and international journals and conferences. His research interests include pollution control, biofuel combustion, alternative fuels, biomass waste management, etc.

Shiva Kumar is an Associate Professor (Senior Scale) in the Department of Mechanical and Manufacturing Engineering at Manipal Institute of Technology, Manipal Academy of Higher Education (MAHE), Manipal, India. MAHE is an outstanding private university having “Institute of Eminence” status declared by the Ministry of Human Resource Development, Government of India. He obtained a doctoral degree from Visvesvaraya Technological University, Belagavi, India, in the area of internal combustion Engines. Dr. Kumar has published more than 50 research papers in national and international journals and conferences. His research interests include engine combustion, alternative fuels for IC engines, refrigeration and air conditioning, heat transfer, solar thermal conversion, CFD studies, and nanofluids.

Marc A. Rosen is a Professor at the University of Ontario Institute of Technology in Oshawa, Canada, where he served as founding Dean of the Faculty of Engineering and Applied Science. Dr. Rosen was President of the Engineering Institute of Canada. A registered Professional Engineer in Ontario, he serves as Editor-in-Chief of several journals and was a Director of Oshawa Power and Utilities Corporation. With over 60 research grants and contracts and 900 publications, Dr. Rosen is active in sustainable energy, environmental impact, and energy technology (including renewable energy and efficiency). Much of his research has been carried out for industry, and he has written numerous books. Dr. Rosen has worked for such organizations as Imatra Power Company in Finland, Argonne National Laboratory near Chicago, and the Institute for Hydrogen Systems near Toronto. Dr. Rosen has received numerous awards and honors and is a fellow of several societies and organizations.

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