

SUSTAINABLE PERFORMANCE: ENHANCING CI ENGINES WITH GREEN-SYNTHESIZED NANOPARTICLES AND BIODIESEL

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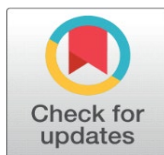
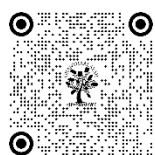
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ABSTRACT

This study investigates the potential of green-synthesized nanoparticles (NPs) doped with a 20% biodiesel blend to enhance the performance and emissions characteristics of a compression ignition (CI) engine. The green synthesis of NPs offers an environmentally friendly alternative to conventional methods, while the addition of biodiesel provides a renewable fuel source. Experimental trials were conducted using various concentrations of NP-doped biodiesel blends in a CI engine. Performance parameters such as brake specific fuel consumption (BSFC), brake thermal efficiency (BTE), and exhaust gas temperature (EGT) were measured. Additionally, emissions profiles, including smoke intensity, carbon monoxide (CO), oxides of nitrogen (NO_x), and unburned hydrocarbons (HC), were analyzed. The results demonstrated that the incorporation of NP-doped biodiesel blends led to significant improvements in engine performance. A reduction in BSFC and an increase in BTE were observed, indicating enhanced fuel efficiency. Furthermore, the NP-doped blends contributed to a substantial decrease in smoke, NO_x and other harmful emissions, suggesting a positive environmental impact. This research highlights the promising potential of green-synthesized NPs and biodiesel blends as a sustainable and efficient fuel alternative for CI engines.

Keywords: Biodiesel, Diesel Engine, Performance, Emission, Nano Particles



1. INTRODUCTION

Climate change is a significant global challenge, with the average global atmospheric carbon dioxide reaching a record high of 412.5 ppm in 2020, despite the economic slowdown caused by the COVID-19 pandemic. The alarming increase in greenhouse gas emissions is causing global surface temperatures and sea levels to rise, leading to abrupt weather patterns and climate change. To mitigate climate change's impact on human habitat, atmospheric greenhouse gas (GHG) concentrations must be reduced (Fankhauser et al., 2022). This can be achieved by reducing sources or improving greenhouse gas sinks, requiring changes in human behavior and adopting alternative energy sources. Decarbonization is one approach, with bioenergy being a versatile fuel source that can reduce emissions due to its CO₂ neutrality (Wu et al., 2023). Bioenergy, or energy derived from biomass, offers numerous technologically mature options that can reduce emissions and address energy access and security concerns if used efficiently, although the efficiency of bioenergy usage varies from site to site (Neupane, 2023).

1.1. INDIAN POLICY ON BIOFUELS

India's bioenergy supply, accounting for 21% of the country's total energy supply, has stagnated compared to fossil fuel growth. The country's transportation energy demand has tripled since 2000. In 2008, India launched the National Action Plan on Climate Change, which added the "National Bio-energy Mission" to promote high capital investment in biomass-based power plants. India has implemented policy initiatives to promote biofuel use, including compulsory fuel blending programs, flex-fuel vehicle rewards, and farmer subsidies. The "National Policy on Biofuels" aims for 20% biofuel blending by 2018, focusing on nonfood feedstocks from deteriorated or insufficient agricultural land. The "National Biodiesel Mission" identifies *Jatropha curcas* as a viable plant oilseed (Roy & Chandra, 2019).

The National Policy on Biofuels in India allows the mixing of ethanol with petrol to reduce oil imports. Ethanol will be produced from damaged food grains, rotten potatoes, corn, and sugar beet. The policy supports the development of procurement mechanisms for biodiesel production from short-duration crops, non-edible oilseeds, and waste cooking oil. The Ministry of Natural Resources and Environment is implementing the "National Biogas and Manure Management Programme" to encourage domestic biogas plants in rural and semi-urban areas (Prasad et al., 2019).

1.2. BIODIESEL PRODUCTION IN INDIA AND SELECTION STRATEGY

The most common commercial conversion process configurations for biodiesel production based on feedstock properties, such as free fatty acid concentration in the feedstock are: Acid catalyzed esterification, Base catalyzed transesterification and Two Step or Mixed process. There are several other methods for producing biodiesel, but the high investment requirements or operating costs have rendered them commercially unviable. The heterogeneous transesterification process in biodiesel manufacture is less commercially recognized but eliminates the need for a catalyst removal unit and reduces the use of reagents and energy. Choosing the right process configuration is complex due to the variety of available processing methods and feedstocks, their composition, and end-use options. There are two methods for configuring biodiesel production: resource-based, where feedstock selection is followed by technology configuration, and technology-based, where feedstock selection is preceded by technology configuration (Bashir et al., 2022).

Figure 1 depicts the selection strategy for biodiesel production. The resource-based method is commonly used for biodiesel production when there is a guaranteed supply of predefined feedstocks, such as acid oil from oil refining industries. The technology options are designed to fit the feedstock's properties, and the process begins with selecting a technology from available options and then choosing a feedstock. This method ensures that the technology is designed to fit the feedstock's properties effectively (Agarwal et al., 2017; Konur, 2021).

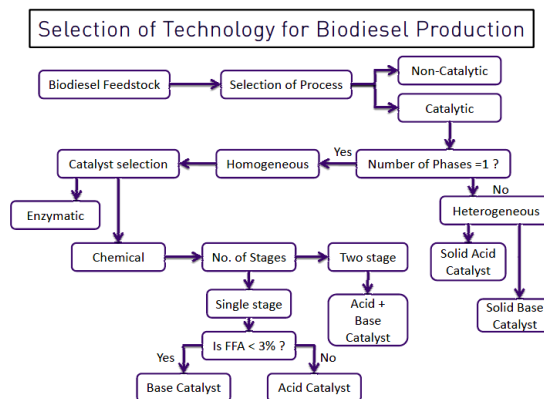


Figure 1 Selection of Technology for production of biodiesel

Biodiesel production involves trans-esterifying oil or fat with low molecular weight alcohols like methanol or ethanol, using an alkaline or acid catalyst. Esterification and transesterification are two common reactions in biodiesel production. Transesterification is a nucleophilic substitution reaction where alcohol attacks the carbonyl group in triglycerides, forming fatty acid alkyl esters and glycerol (Ogunkunle & Ahmed, 2019).

1.3. PREPARATION OF BIODIESEL

The alcohol-catalyst mixture is mixed with catalysts like H_2SO_4 or HCl , and oil is added to the mixture. The transesterification reaction occurs in a closed environment to minimize loss, with the temperature kept below the alcohol's boiling point. Surplus alcohol is used for oil conversion, while excess alcohol can be recovered later. The process results in the formation of biodiesel and glycerol, which are separated using gravity settling vessels or centrifugal separation. The glycerol phase is denser, while the biodiesel phase is lighter. Alcohol is used in the biodiesel and glycerol phases, requiring recovery through distillation or flash evaporation processes. The mixture is neutralized to prevent excess catalyst presence. Biodiesel contains glycerol, alcohol, and a catalyst, which can reduce fuel lubricity, cause injector choking, and cause health risks. To remove these impurities, biodiesel is washed 4-6 times with warm water at $40\text{--}50^\circ\text{C}$, avoiding soap formation, and avoiding the presence of alcohol residues. After the washing, Biodiesel must be dried. Then only it can be used in a diesel engine. The biodiesel is simply heated to 110°C so that water content evaporates and biodiesel becomes free of water (Esmaeili, 2022).

1.3.1. THE VARIATIONS OF SIGNIFICANT INPUT PARAMETERS

The biodiesel production configurations are significantly influenced by various input parameters, such as the alcohol to oil molar ratio. Higher ratios improve miscibility and contact between alcohol molecules and triglyceride, leading to increased biodiesel conversion efficiency, yield, and production cost. The reaction temperature, determined by the feedstock and reagent conditions, is maintained below the boiling point of the alcohol used. Most studies report reaction temperatures of 60°C , which is a few degrees below the boiling point of methyl alcohol and ethyl alcohol. Reaction time refers to the time it takes for reactants to transform into products in a reactor, with low times allowing more output per unit time. Catalyst concentration, which requires less activation energy, reduces reaction time (Chozhavendhan et al., 2020).

Bioenergy is a promising alternative for reducing greenhouse gas emissions and promoting renewable energy adoption. However, long-term resource competition and threats to biodiversity conservation hinder its widespread use. Biodiesel, a low-cost engine fuel with excellent lubrication properties, has a safe flash point of 150°C . However, it has drawbacks like lower heating value, lower brake thermal efficiency, poor cold flow, increased NO_x emissions, and reduced shelf life. Despite these, biodiesel is a carbon-neutral engine fuel, offset by CO_2 absorbed by feedstock plantation, making it a superior alternative to mineral diesel. Policy development should consider these potential resource conflicts and unforeseen effects (Callegari et al., 2020).

1.3.2. SELECTION OF BIODIESEL AND NANOPARTICLE FOR CI ENGINE

Cottonseed oil (CSO), a byproduct of the cotton industry, can be processed into biodiesel, a renewable fuel alternative to traditional fossil fuels. Biodiesel made from cottonseed oil offers several advantages. Cottonseed oil is a sustainable and readily available resource, reducing dependence on fossil fuels. Higher oxygen content in the CSO biodiesel results in lower emissions of harmful pollutants like particulate matter, carbon monoxide, and sulfur oxides (K. D. [1] Chaudhari et al., 2016). Using cottonseed oil for biodiesel production can support local farmers and boost the agricultural economy. Use of CSO Biodiesel fuel can improve engine performance by addressing issues like low brake thermal efficiency, increased fuel consumption, and exhaust emissions (Ganesan et al., 2020; Kumar et al., 2023). Nanoparticles, with benefits like improved dispersion, air-fuel mixing, and oxygen content, have been tested as fuel additives, resulting in shorter ignition delays, higher combustion enthalpy, and faster heat release rates. However, controlling nanoparticle size, shape, and porosity during synthesis is challenging (Kiran et al., 2021).

Nanoparticle synthesis techniques are broadly classified into two types: one-step and two-step methods. One-step synthesis involves mixing nanoparticles and base solution at the same time, eliminating the need for drying, preservation, and dispersion, resulting in a cost-effective and long-lasting nanofluid. Metal oxides such as aluminum, cerium, titanium, and copper have been investigated for use as nanoparticle fuel additives to reduce engine emissions. These oxides add oxygen to the combustion chamber, which reacts with incomplete combustion byproducts, increasing heat release and combustion efficiency. Cerium oxide (CeO₂) nanoparticles used as fuel acted as catalysts, resulting in enhanced combustion. The study successfully reduced BSFC, NO_x emissions, and smoke opacity by 2.5%, 15.7%, and 34.7%, respectively (Upadhyay et al., 2024). Sarma et al. (Jit Sarma et al., 2023) discovered that using titanium oxide (TiO₂) nanoparticles as an additive reduced CO, HC, and NO_x emissions by 46.56 percent, 28.4%, and 2.3%, respectively. According to studies, using biodiesel blends with copper oxide CuO nanoparticles in biodiesel-fueled engines resulted in better combustion, improved performance characteristics, and reduced exhaust emissions (Arun et al., 2023; Jegan et al., 2023; Singh Pali et al., 2023). Researchers experimented with aluminum oxide nanoparticles (Al₂O₃) as fuel additives and discovered that the increased engine efficiency is due to the nanoparticles' higher surface-to-volume ratio and thermal conductivity. The nanoparticles act as a chemical catalyst during combustion, increasing the rate at which fuel is burned. The analysis also revealed that NO_x formation increased and carbon monoxide and unburned hydrocarbon emissions decreased (Prabu, 2018; Sundar et al., 2022).

The study explores the use of metal oxide nanoparticles in improving biodiesel-fueled CI engine performance using a green synthesis method using fruit peel or plant leaf extract. The nanoparticles act as catalysts, increasing combustion efficiency and reducing harmful pollutants.

2. METHODOLOGY

2.1. MATERIALS AND METHODS

The study makes use of 98% pure calcium nitrate (Ca(NO₃)₂), magnesium nitrate (Mg(NO₃)₂), sodium hydroxide NaOH, and deionized water Grade-I, as well as *Murraya Koenigii* leaves (also known as curry leaves) and *Citrus aurantium* (sour orange) fruit peels from a local farm.

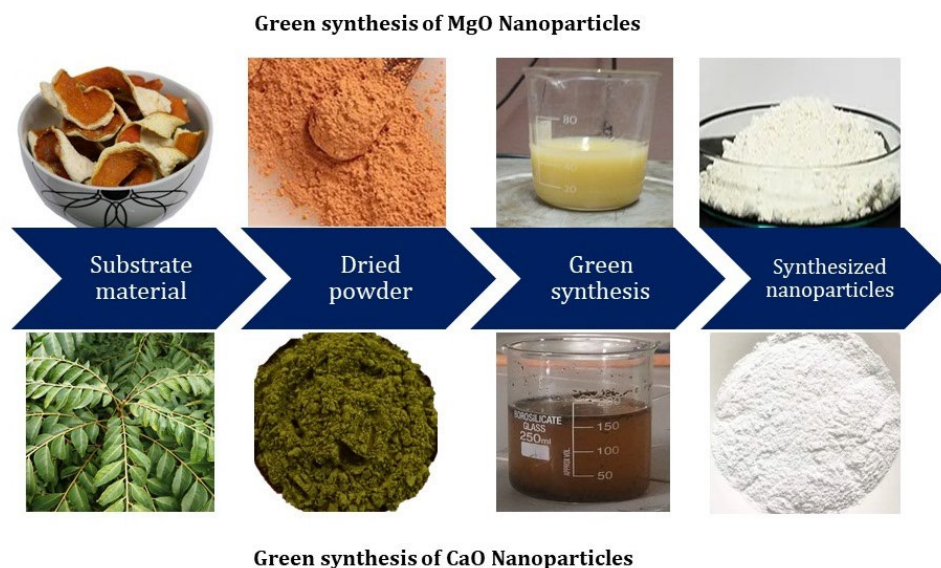


Figure 2 green synthesis of CaO and MgO nanoparticle using biological substrates.

The process of creating an aqueous extract of *Citrus aurantium* fruit peels is illustrated in Figure 2. The orange peels are cut, washed, dried, and boiled in distilled water to produce a light brown extract. The extract is then strained and stored at 4°C. The extract is then poured into a magnesium nitrate solution, stirred for 12 hours, and then centrifuged. The precipitate is then filtered, washed, and oven-dried at 70°C for 2 hours. Magnesium oxide nanoparticles are obtained by calcination in a muffle furnace at 400°C for three hours and allowed to cool off overnight (Vijayakumar et al., 2022).

The collected *Murraya Koenigii* leaves are washed twice with deionized water to remove impurities, dried in an oven at 80°C for 2 hours, and then boiled for 30 minutes in distilled water to obtain a light brown extract. The solution is filtered using Whatman filter paper No. 1 to remove any impurities, and the leaf extract is stored at 4°C for further use. A solution of 0.5 M calcium carbonate and 50 ml *Murraya Koenigii* leaf extract is stirred until it reached 60°C. The solution is then added to 0.5 M NaOH solution, resulting in the formation of calcium hydroxide particles. The precipitate is filtered, washed with distilled water, and dried in an air oven at 110°C. Calcium oxide nanoparticles are obtained by calcination in a muffle furnace at 400°C for three hours and allowed to cool off overnight.

2.2. CHARACTERIZATION STUDIES ON SYNTHESIZED NANO PARTICLES

The structural characterization of the synthesized nanoparticles is obtained by using UV-Vis, FTIR, and SEM-EDX. FTIR studies are performed using Bruker Alpha-II FTIR spectrometer and optical absorbance spectral studies are done using Cary 60 UV-VIS spectrophotometer. SEM and EDX studies are also carried out using FEI – NOVA NANO 450 scanning electron microscope.

The UV visual spectroscopic study found poly-phenolic bioactive compounds in *Murraya Koenigii* leaf extract, which reduces calcium ions to calcium oxide nanoparticles. The absorption spectra show a peak at 211 nm and 275 nm, indicating the formation of nanoparticles as seen in figure 3(a). The FT-IR spectrum in figure 3(b) shows a broad absorption band at 3437 cm⁻¹, indicating alcohol/phenol –OH stretching vibration, carboxylic acid –OH stretch, and N-H stretching of amides. SEM micrographs in figure 3(c) reveal cylindrical, granular, and nano-sized CaO nanoparticles with average particle sizes of 30-70 nm. Energy dispersive X-ray (EDX) analysis confirmed the elemental composition, showing peaks due to Ca and O with a weight percentage of 45.77 and 54.23%, respectively. The synthesized material is highly pure, with peaks due to Ca and O (Sudarsanam & Jayaprabakar, 2024).

The study examined the synthesis of MgO nanoparticles using UV-Vis absorption spectrum and FTIR spectrum. A broad absorption peak at 290 nm confirmed the formation of biosynthesized MgO nanoparticles in shown figure 3(d). The FTIR spectrum in figure 3(e) shows the presence of a hydroxyl group in the spectrum, with peaks at 3416.26, 1481, and 679.8 cm⁻¹ attributed to O–H stretching vibrations, bending vibrations of water molecules, and surface hydroxyl group (–OH) and stretching vibration mode for the Mg–O–Mg modifying range. SEM micrographs in figure 3(f) reveal the surface morphology of MgO nanoparticles, which are spherical, granular, and nano-sized. The average particle size

ranges between 100-120 nm. The FESEM image shows an average particle size of 100-120 nm. The EDX spectrum shows the synthesized material is highly pure, with peaks due to Mg and O. The weight percentage of Mg and O was 46.4 and 53.6%, respectively (Abinaya et al., 2021).

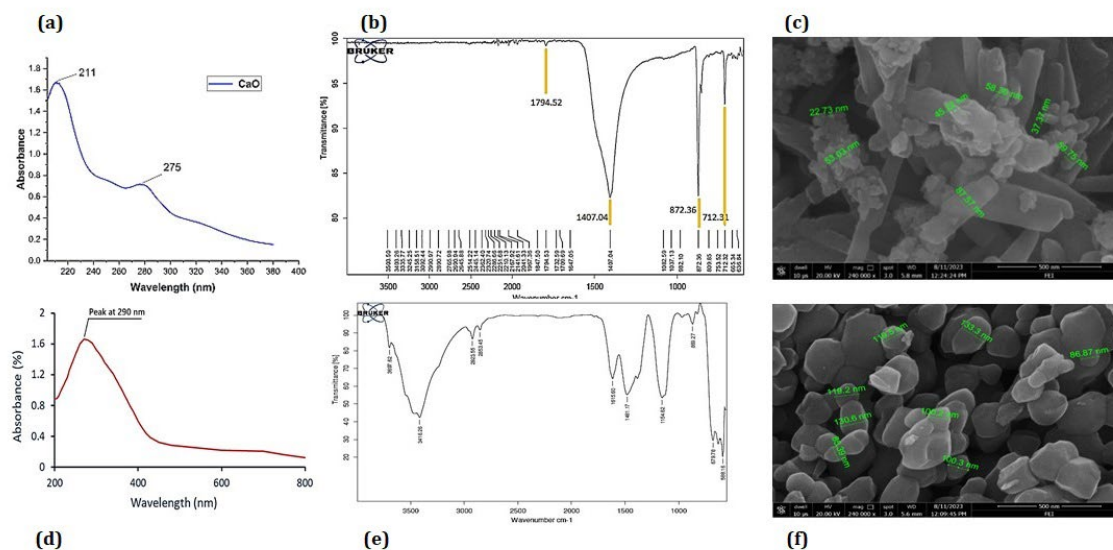


Figure 3 Results of characterization study on synthesized CaO and MgO nanoparticles

2.3. EXPERIMENTAL SETUP

The study employs four fuel samples that contain pure diesel(B0), 20% biodiesel in diesel (B20), and a B20 blend with 100 ppm CaO nanoparticles (B20C100) and 100 ppm MgO nanoparticles (B20M100), respectively. Previous research indicates that 20% biodiesel blended fuel provides optimal engine performance (K. Chaudhari et al., 2023). Experimental studies compare fuel sample performance and emission parameters under various loading and steady-state conditions. The experimental setup which study employs, as shown in figure 4, shows an engine-load cell configuration featuring a 3.5 kW Kirloskar compression ignition engine and a piezoelectric load cell. The test rig is dual fuel capable and includes EngineSoft software for recording observations. All trials are carried out with a constant engine speed of 1500 rpm and varying engine loads. Emission parameters are measured with the AVL Digas 444N gas analyzer and the AVL 437C smoke meter.

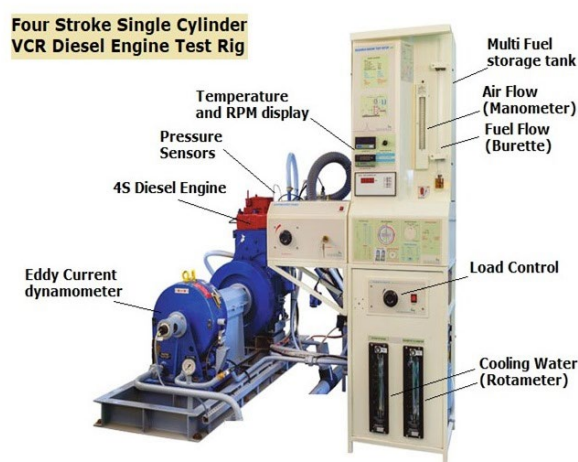


Figure 4 Experimental setup of VCR diesel engine test rig and accessories.

3. RESULTS AND DISCUSSION

The performance parameters in this study, as shown in figure 5, using the diesel fuel and used cooking oil biodiesel blend B20 as a reference for comparison are discussed here. Diesel fuel offers highest BTE among all fuels, due to its high calorific value. Addition of NPs improves BTE & BSFC of B20 blend marginally by 1.4% and 2.3% for CaO and MgO additives respectively. Higher BTE of diesel fuel results in lowest EGT among all fuels. NP addition reduces EGT for B20 blend. As a result, NO_x emissions are reduced by 3.5% and 4.7% for CaO and MgO additives respectively, as shown in figure 7.

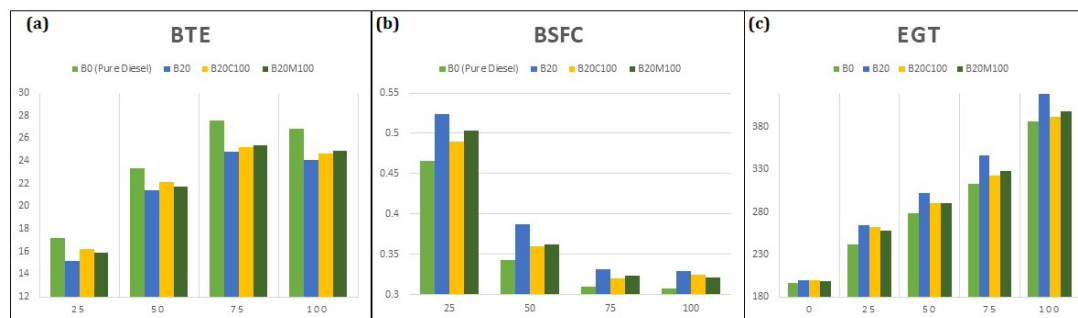


Figure 5 Performance behavior of CI engine with varying engine load and fuel blends.

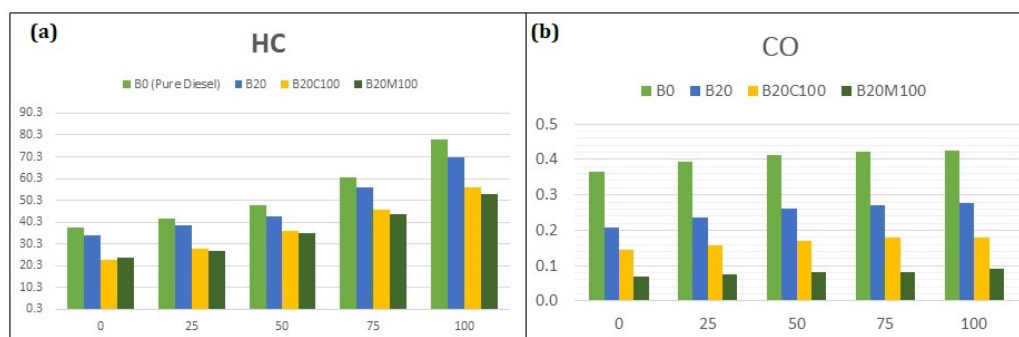


Figure 6 Unburnt HC and CO Emission behavior with varying engine load and fuel blends.

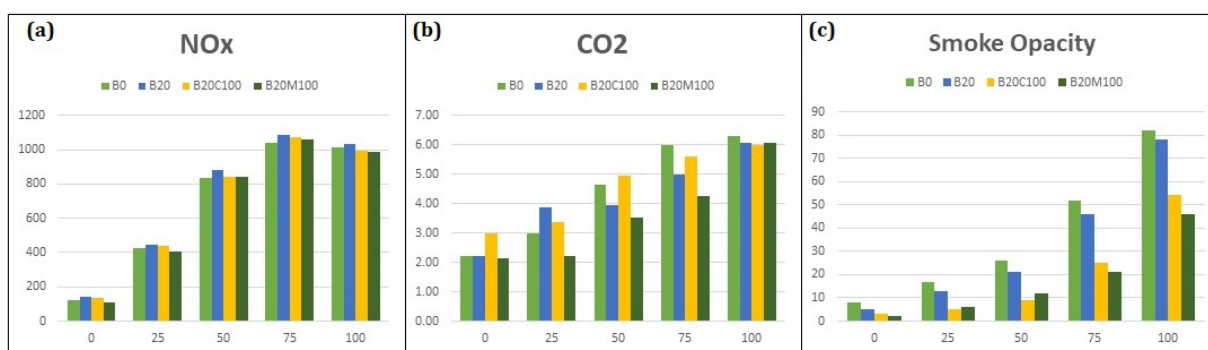


Figure 7 NO_x, CO₂, and Smoke Emission behavior with varying engine load and fuel blends.

CaO NPs result in lower HC & CO emission by 20% and 16% while MgO NPs result in lower HC & CO emission by 24% and 25% compared to B20 fuel as evident from figure 6. Soot formation is significantly reduced by 34% and 44% for CaO and MgO additives respectively. This occurs due to extra oxygen available and improved combustion due to better atomization and micro explosion. It is concluded that CaO and MgO addition in biodiesel blend significantly lowers emission levels as opposed to diesel and other tested fuels.

4. CONCLUSION

The results showed that using NP-doped biodiesel blends resulted in significant improvements in engine performance. A decrease in BSFC and an increase in BTE were detected, indicating improved fuel efficiency. Furthermore, the NP-doped blends contributed to a significant reduction in smoke, NO_x, and other harmful emissions, indicating a favorable environmental impact. This study emphasizes the promising potential of green-synthesized nanoparticles and biodiesel blends as a sustainable and efficient fuel alternative for CI engines. In future, nanoparticle additives can be tested with higher blends like B40.

CONFLICT OF INTERESTS

None.

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None.

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