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The effect of adding green synthesized and commercial silver nanoparticles to biodiesel on diesel engine performance and emissions

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ABSTRACT

This study evaluates the impact of silver nanoparticles synthesized via a green method using *Humulus lupulus* L. and commercial silver nanoparticles (CAS: 7440-22-4) on biodiesel performance and emissions in diesel engines. Biodiesel from waste cooking oil was tested under partial load (1–4 kW) with the following blends: 100 % diesel (D), 50 % diesel-50 % biodiesel (BD50), biodiesel with green-synthesized nanoparticles (200, 400, 600 ppm: B_G200, B_G400, B_G600), and biodiesel with commercial nanoparticles (200, 400, 600 ppm: B_C200, B_C400, B_C600). The results showed that green-synthesized nanoparticles significantly reduced CO emissions (up to 71.42 % at 4 kW for B_G600), HC emissions (48.88 %), and particulates. Combustion efficiency improved, increasing CO_2 emissions (peak 2.59 % for B_G600 at 4 kW). However, exhaust temperatures rose (583 °C for B_G600), and NO_x emissions increased, peaking at 237 ppm for B_G400 at 4 kW. Green nanoparticles were more effective than commercial ones in reducing CO, HC, and particulate emissions while enhancing combustion. However, increased CO_2 and NO_x emissions suggest the need for further optimization. This study highlights green nanotechnology's potential to improve biodiesel performance sustainably while addressing environmental challenges.

1. Introduction

The need for energy is steadily rising due to global population growth, technological advancements, and improved living standards. As for energy use, gasoline and diesel fuel are used, especially in transportation. According to the statistics of 2021, approximately 82.7 million vehicles were sold. Approximately 26.3 million of this was realized commercially [1]. There are approximately 1.3 billion land vehicles worldwide. Due to emission standards, diesel engines have not been produced in passenger cars. However, giving up on commercial vehicles, especially heavy ones, is difficult. In order to reduce carbon emissions, electric vehicles are starting to become widespread. However, it is thought that it will remain at a limited level due to the countries' lack of battery, range and electricity infrastructure.

For this reason, studies on diesel engines continue, especially to reduce emissions. Low carbon emissions or cheaper fuel research

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are increasing daily [2]. In this context, ongoing research is being conducted on incorporating nanoparticles into diesel fuel [3]. Utilizing nanoparticles has been shown to improve combustion efficiency and reduce emissions, according to earlier research [4–9].

Recently, a significant increase in the popularity of nanotechnology. This technology's utilization spans various fields, including medicine, the electrical sector, pharmaceutical applications, energy production systems, and material production methods [10]. Metallic nanoparticles, which are in the field of nanotechnology, are also used in energy storage transmission with their important properties related to high surface-to-volume ratio [11]. Chemical, physical or biological methods could synthesize metallic nanoparticles. Chemically synthesized nanoparticles are hazardous to the environment because they produce hazardous compounds during and after synthesis [12]. Therefore, as an alternative technique to chemical and physical synthesis methods, the biological synthesis (green synthesis) has been developed [13,14]. In the green synthesis technique, plants and various microorganisms produce metallic nanoparticles. Since plants are easily accessible and widely available, their use in nanoparticle synthesis enables very economical, fast, and stable production [15]. *Humulus lupulus* L. is an herbaceous plant species from the Cannabaceae family, with greenish-white flowers, 2–5 m high, with a yellowish stem [16]. It has many biological activities and nanoparticle synthesis potential with valuable phytochemicals it contains, such as humulone and its derivatives, phenolics, and terpenes [16].

Nanoparticles, including various metallic elements such as Ag, Cu, Mg, Mn [17], as well as semi-metals like boron and metal oxides like Al_2O_3 [18], CeO_2 [19], CuO [20], MgO [21], Mn_2O_3 [22], Co_3O_4 [22], TiO_2 [23], ZnO [24], have the potential to serve as supplementary components in diesel engines [25]. The carbon based nanoparticles in question exhibit dimensions that span from 1 to 100 nm and possess the ability to generate energy through the process of combustion [26].

Afzal and his associates investigated how diesel engine performance and emissions were affected by biodiesel, silver nanoparticles, and scum oil alcohol. The main objectives of this study were to find the ideal diesel to biodiesel blend ratio, assess the impact of adding silver nanoparticles to a 60 % diesel-biodiesel mixture, and compare the performance results of pure diesel fuel with blends of biodiesel and alcohol. These evaluations were conducted under varying injection pressures and crank angles. According to their research, using silver nanoparticles reduced pollutants while having no discernible impact on engine performance [27]. Saraee et al. conducted a study to determine how adding silver nanoparticles to diesel fuel affects emissions and engine performance. Silver nanoparticles were added to diesel fuel in their study at 10, 20, and 40 parts per million (ppm). Their experiment revealed a significant decrease in emissions when silver nanoparticles were included. Furthermore, they observed enhancements in combustion and thermal efficiency, accompanied by a reduction in fuel consumption. Including nanoparticles in diesel fuel generally shows promise for enhancing engine efficiency and reducing emissions. More research is required to completely comprehend the impacts of various nanoparticle forms and concentrations on diesel engines [28]. Yuvarajan and their team conducted studies to explore the effects of incorporating silver oxide at concentrations of 5 and 10 ppm into palm oil biodiesel fuel. These studies were conducted in a diesel engine operating at various power levels while keeping the constant speed. The trials yielded findings indicating that the use of silver oxide improved thermal efficiency and reduced specific fuel consumption. Additionally, the application of this technology led to improvements in emissions, including reductions in carbon monoxide (CO), nitrogen oxides (NOx), hydrocarbons (HC), and smoke [29]. Yilmaz et al. determined the best fuel combinations for waste oil-derived diesel, pentanol, and biodiesel using the Response Surface Methodology (RSM) technique. They discovered that the blend that performed best, with a high R2 value, was made up of 12.58 % pentanol, 8.33 % biodiesel, and 79.09 % diesel. Additionally, their research investigated engine performance and emissions by adding n-butanol, n-propanol and 35 % n-butanol alcohols to biodiesel and diesel. Their study reduced toxic emissions when n-butanol was added to diesel and biodiesel fuels [30,31]. Using simulation software, Temizer and their team conducted a numerical investigation into including ethanol and diethyl ether to diesel fuel. By including ethanol, they observed increased NO emissions and improvement in turbulent kinetic energy [32]. Firat et al. examined the effects on engine performance and emissions of ethanol and diesel fuels in dual direct injection and RCCI modes, contrasting the outcomes with those of standard diesel. In RCCI mode, they noted a greater increase in thermal efficiency compared to the dual direct injection system. They observed significant reductions in CO and HC emissions with the dual direct injection system, in addition to improvements in NO_x and smoke emissions in both the RCCI and dual direct injection modes [33]. Najafi studied the effect on emissions and engine performance by including silver and carbon nanotube nanoparticles at 40, 80, and 120 ppm concentrations to biodiesel in a diesel engine. Their study showed that silver nanoparticles increased the engine performance, while carbon nanotubes exhibited even greater performance enhancements. Combining carbon nanotubes with silver nanoparticles in biodiesel not only reduced fuel consumption but also further decreased emissions. Carbon nanotubes showed superior results compared to silver nanoparticles, except for HC emissions [34]. Murugan and their team conducted experimental tests involving the addition of green-synthesized silver nanoparticles to Manilkara Zapota biodiesel fuel in a diesel engine, testing concentrations of 40, 80, and 120 ppm. The results indicated that adding 80 ppm silver nanoparticles yielded the best engine performance and emissions results, particularly when blended with a mixture of 80 % diesel and 20 % biodiesel [35]. Nayak et al. added silver nanoparticles, produced through green synthesis from *Santalum album* plant fibers, into biodiesel fuel at 25 and 50 ppm concentrations. They estimated engine performance and emissions using the RSM method [36]. Uyaroglu et al. blended organic manganese and biodiesel with diesel fuel to study engine performance and emissions. According to their research, the thermal efficiency of diesel fuel was enhanced by the addition of organic manganese and biodiesel. However, it also resulted in increased fuel consumption [37]. Zhou et al. conducted numerical studies on the addition of ozone to biodiesel fuel in an HCCI engine, developing a reduced chemical kinetic mechanism for this purpose. They observed that ozone had a significant effect on auto-ignition [38]. Chacko and Jeyaseelan investigated how adding graphene oxide and nanoplatelets to diesel and biodiesel fuel affected engine performance and emissions. They found that graphene oxide was particularly effective in reducing smoke emissions, while graphene nanoplatelets produced better results in other emissions [39]. Liu et al. explored the impact of adding palm oil biodiesel to diesel fuel in a common rail injection system. They observed a significant decrease in HC, CO, and soot emissions and an increase in NO_x emissions when biodiesel was added [40]. Murugesan and their team investigated engine performance and emissions by incorporating green-synthesized silver nanoparticles from neem plant fibers into biodiesel and diesel fuel mixtures. Their findings showed increased thermal efficiency, maximum pressure, and heat release rate with the addition of silver nanoparticles. In addition, there was an increase in NOx emissions coupled with a decrease in CO, HC, and particle emissions [41].

Despite significant advancements in biodiesel research, several challenges persist. Existing studies primarily focus on the effects of metallic nanoparticles as fuel additives; however, there is a notable gap in comparative investigations of green-synthesized versus commercially available nanoparticles, particularly silver nanoparticles. Additionally, most studies, such as those referenced in Refs. [42–45], limit nanoparticle concentrations to 100 ppm, leaving the effects of higher concentrations unexplored. The environmental and performance impacts of green synthesis methods, which use sustainable materials like plants, also remain underrepresented in the literature.

This study addresses these gaps by synthesizing silver nanoparticles (HL-AgNPs) through a green method using *Humulus lupulus* L. (hops) and comparing their effects with commercially available silver nanoparticles. By testing fuel blends containing diesel, biodiesel, and biodiesel with silver nanoparticles at concentrations of 200 ppm, 400 ppm, and 600 ppm, this research investigates the effects of higher nanoparticle concentrations on engine performance and emissions. Experiments were conducted under diverse load conditions (1–4 kW) at a consistent engine speed, measuring critical parameters such as in-cylinder pressure, exhaust gas temperature, and emissions (CO, HC, NO_x, CO_2, and particulate matter).

The novelty of this work lies in its commitment to environmental sustainability through green synthesis of nanoparticles and its innovative approach of exploring higher nanoparticle concentrations for performance optimization. By bridging the gap in comparative analysis and expanding the scope of nanoparticle concentrations, this study contributes valuable insights into improving biodiesel's efficiency and environmental profile. These findings align with and extend the current body of knowledge in studies like [46, 47] and others referenced.

2. Materials and methods

2.1. *Extraction of Humulus lupulus L., green Syhtesis and characterization of HL-AgNPs*

The scientific name of the plant commonly known as hops is *Humulus lupulus* L. The item was acquired from Bilecik, Türkiye, in the year 2020. The plant samples underwent a drying process and were subsequently subjected to extraction using a water-to-sample ratio of 1:10 for a duration of 72 h. Following extraction, the samples were filtered. The synthesis of silver nanoparticles was conducted using the methodology outlined in reference [48]. In order to achieve this objective, a water extract derived from the plant species *Humulus lupulus* L. is utilized. The solution was combined with a 5 mM silver nitrate ($AgNO_3$) concentration and subsequently agitated. The observation of a transition in colour to a dark brown hue was recorded. The presence of silver nanoparticles was confirmed through UV absorption scanning within the wavelength range of 250 nm–750 nm. The synthesized silver nanoparticles, also known as HL-AgNPs, were subjected to various characterization techniques to assess their properties. These techniques included using a UV-spectrophotometer to analyse their absorption spectra, FTIR-ATR to identify the functional groups present, and SEM to examine the particle size and morphological features.

2.2. *Test fuel*

Diesel fuel was purchased from OPET company, which sells products commercially. Biodiesel was produced from waste oil obtained from Muş Alparslan University Cafeteria. The obtained waste oils were first subjected to filtration. After filtration, it was heated to 110 °C to clean the water inside, and the waste oils were rested. Biodiesel from pre-treated waste oils is planned to be produced using the transesterification method. For this purpose, 20 % by volume of ethyl alcohol and 3 % by mass of sodium hydroxide were added to the pre-treated waste oils. The new mixture was reacted at 65 °C for 4 h in a heater with a magnetic stirrer. Thus, the first stage of biodiesel production was completed. The reaction products obtained were separated from the rested glycerin in the separating funnel, and the washing process was started. The washing process was repeated more than once. Biodiesel pH was measured after each washing process. The resulting mixture was rested in the separating funnel again, and the biodiesel production process was completed by heating it up to 110 °C to remove the water in it. The technical specifications of the produced biodiesel and commercially purchased diesel fuel are given in Table 1.

The fuel mixture BD50 (50 % diesel fuel + 50 % biodiesel fuel) used in the engine experiments was prepared by volume. Commercially available silver nanoparticles and green-synthesized silver nanoparticles, derived from *Humulus lupulus* L., were added

Table 1
Diesel and biodiesel fuel properties.

Properties	Diesel	Biodiesel
Lower heating value (kJ/kg)	43010	39600
Kinematics viscosity (mm^2/s), at 40 °C	3.4	5,69
Density (g/cm^3) at 15 °C	0.834	0.853
Flash point (°C)	66	92
Cetan number	52	53
Oxygen (%, w)	0	%50

to 100 % biodiesel (B). The silver nanoparticles were accurately measured using a precision balance (±0.0001 g) and incorporated into the biodiesel at concentrations of 200 ppm, 400 ppm, and 600 ppm. These mixtures were labeled as B_C200, B_C400, B_C600 (for biodiesel with commercial nanoparticles) and B_G200, B_G400, B_G600 (for biodiesel with green-synthesized nanoparticles). The obtained new fuel blends were mixed in an ultrasonic mixer at 40 hz waves for 1 h and immediately used in the engine. Table 2 provides the detailed technical properties of these fuel blends.

2.3. *Experimental test Procedure*

A single-cylinder direct-injected compression ignition engine was used for the experimental study. The engine in question operates on a four-stroke cycle, naturally aspirated, and relies on air cooling for temperature regulation. Table 3 presents the primary attributes of the utilized diesel engine.

The experimental investigation consisted of conducting operations at a rotational speed of 3000 revolutions per minute (rpm) for all the fuels. Each fuel combination was subjected to testing at this particular speed while being exposed to different engine loads ranging from 1 kW (kW) to 4 kW (kW). Power levels (in kW) were used on the x-axis for all figures to provide an intuitive and consistent representation of engine operating conditions. This approach aligns with standard practices in engine performance studies and ensures direct applicability to similar engines. The measurement of fuel consumption involved the determination of the duration required for the consumption of 10 g of fuel, utilizing an electronic balance with a precision of 0.01 g. In order to quantify the pressure within the cylinder, a Piezo resistor Kistler 4065B0200DS1 air-cooled pressure sensor was employed, and the signals emitted by the sensor were enhanced by the utilization of a charge amplifier (Kistler 4624AK21). In addition, an Oprant AutoPSI-A type air-cooled pressure sensor was employed to quantify the pressure within the fuel line. The FNC 50B incremental optical encoder was employed to determine the precise location of the crankshaft.

The data collected from the sensors was continuously watched and recorded in real-time utilizing a 4-channel PicoScope 2406B oscilloscope. In order to get the pressure values for both the in-cylinder and fuel line, an average of 100 cycles was recorded with a precision of 0.5 crank angle (CA). The heat release rate was determined by employing a series of 100 consecutive averages of in-cylinder pressure while disregarding losses and leaks. The heat release rate for each crank angle was determined by using Equation (1) [49].

$$\frac{dQ}{d\theta}=\frac{k}{k-1}\left(P\frac{dV}{d\theta}\right)+\frac{1}{k-1}\left(V\frac{dP}{d\theta}\right) \tag{1}$$

In this equation, $dQ/d\theta$ represents the heat release rate, measured in Joules per crank angle (J/CA), k is the ratio of specific heats, often denoted as C_p/C_v, P represents the cylinder pressure, typically measured in Pascals (Pa), V denotes the variable cylinder volume, measured in cubic meters (m^3). This equation is used to describe the relationship between these parameters in the context of engine performance and combustion analysis. It helps in measuring the rate at which heat is emitted from an engine cylinder during combustion.

The exhaust gas temperature was measured using a K-type thermocouple. Using the Mobydic 5000 COMBI exhaust gas analyzer, the levels of smoke, CO, CO_2, and HC were measured. Table 4 contains the exhaust emission device's comprehensive technical specs. Fig. 1 depicts the schematic depiction of the experimental test setup.

3. Results

The research findings indicated that HL-AgNPs demonstrated the highest level of absorbance at approximately 450 nm [48]. The process of Ag + ion reduction into silver nanoparticles when reacting with *Humulus lupulus* L. The confirmation of the extract was achieved through the observation of alterations in color. The instruments used in this study include a UV–Vis Spectrophotometer (DR/4000U, Hach, Germany), an FTIR Spectrometer (Thermo Fisher Scientific, USA), and a Scanning Electron Microscope (ZEISS Supra 40 VP, Germany) equipped with Energy Dispersive X-ray Spectroscopy (EDX) for elemental analysis. The SEM analysis (Fig. 2 [48]) revealed that the size of the nanoparticles obtained fell within the range of 30.60 nm–36.72 nm.

Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR) spectroscopy was employed to identify the characteristic

Table 2
Certain characteristics of test blends and fuels.

Properties	D	BD50	B_C200	B_C400	B_C600	B_G200	B_G400	B_G600	Standar Method
Kinematics viscosity (mm^2/s), at 40 °C	3.4	5.12	5.73	5.94	5.76	5.92	6.02	6.17	ASTM D445
Density (g/cm^3) at 15 °C	0.834	0.841	0.854	0.865	0.874	0.862	0.873	0.882	ASTM D4052
Lower heating value (kJ/kg)	42440	41020	39700	39900	40200	39700	39900	40200	ASTM D240
Flash point (°C)	60	85	90	85	69	91	84	76	ASTM D93

Table 3
Technical properties of exhaust emissions device.

Emissions	Precision	Range	Resolution
CO_2 (% vol)	±0.5 %	0–20	0.01
CO (% vol)	±1 %	0–10	0.01
Smoke opacity (%)	±2	0–20	0.01
HC (ppm)	±12	0–20000	1

Table 4
Technical properties of exhaust emissions device.

Emissions	Precision	Range	Resolution
CO_2 (% vol)	±0.5 %	0–20	0.01
CO (% vol)	±1 %	0–10	0.01
Smoke opacity (%)	±2	0–20	0.01
HC (ppm)	±12	0–20000	1

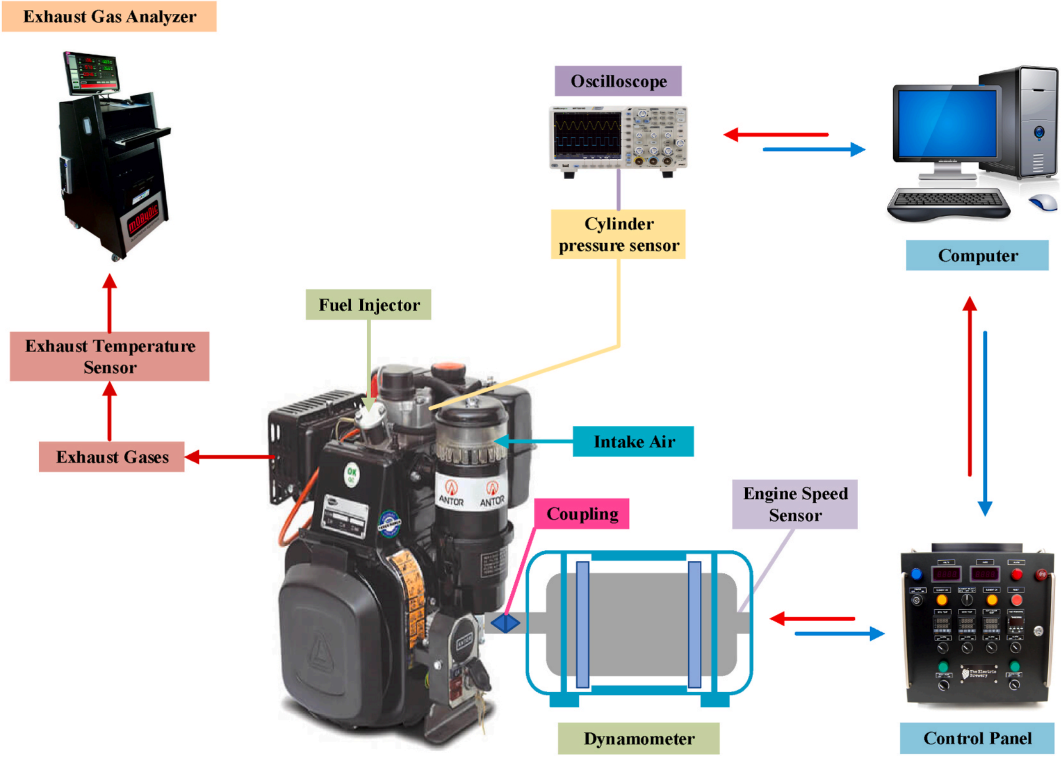

Fig. 1. Experimental setup.

peaks of the aqueous extract and HL-AgNPs. The results revealed that the synthesized nanoparticles displayed distinct peaks at 2296.89 cm^{-1}, 1161.05 cm^{-1}, and 1112.34 cm^{-1}, which were not observed in the aqueous extract. Furthermore, shifts in other peaks were also observed, as depicted in Fig. 3. The spectral region ranging from 3200 to 3400 cm^{-1} was found to be associated with the O—H stretching groups of amides plane bonding, whereas the spectral region spanning from 1650 to 1800 cm^{-1} was designated for the $C=O$ stretching. Also the peaks were numbered and summarized in Table 5.

The limitations of this study include its focus on partial load conditions, the exclusion of long-term engine durability tests, and the lack of economic analysis for nanoparticle production. These areas present opportunities for future research. However, the study's strengths lie in its innovative use of green synthesis for nanoparticles, comparative evaluation of green and commercial nanoparticles, exploration of higher nanoparticle concentrations, and comprehensive analysis of engine performance and emissions. These contributions advance the understanding of biodiesel enhancement and its environmental and performance benefits.

In diesel engines, the timing of the maximum in-cylinder pressure is crucial, and ideally, it should occur as close as possible to the upper dead point. These parameters can vary based on factors like fuel viscosity, density, thermal value, flash point, and cetane number

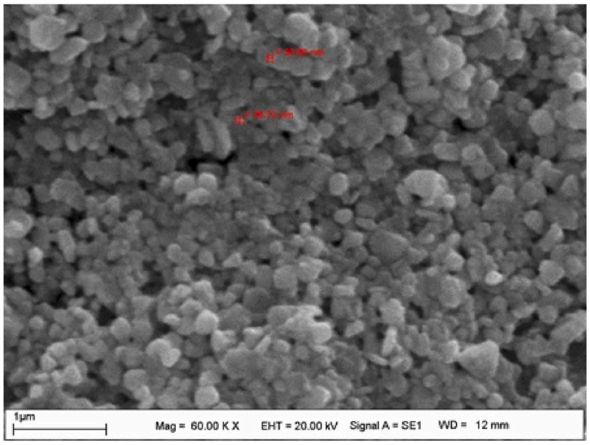

Fig. 2. SEM images of HL-AgNPs [48].

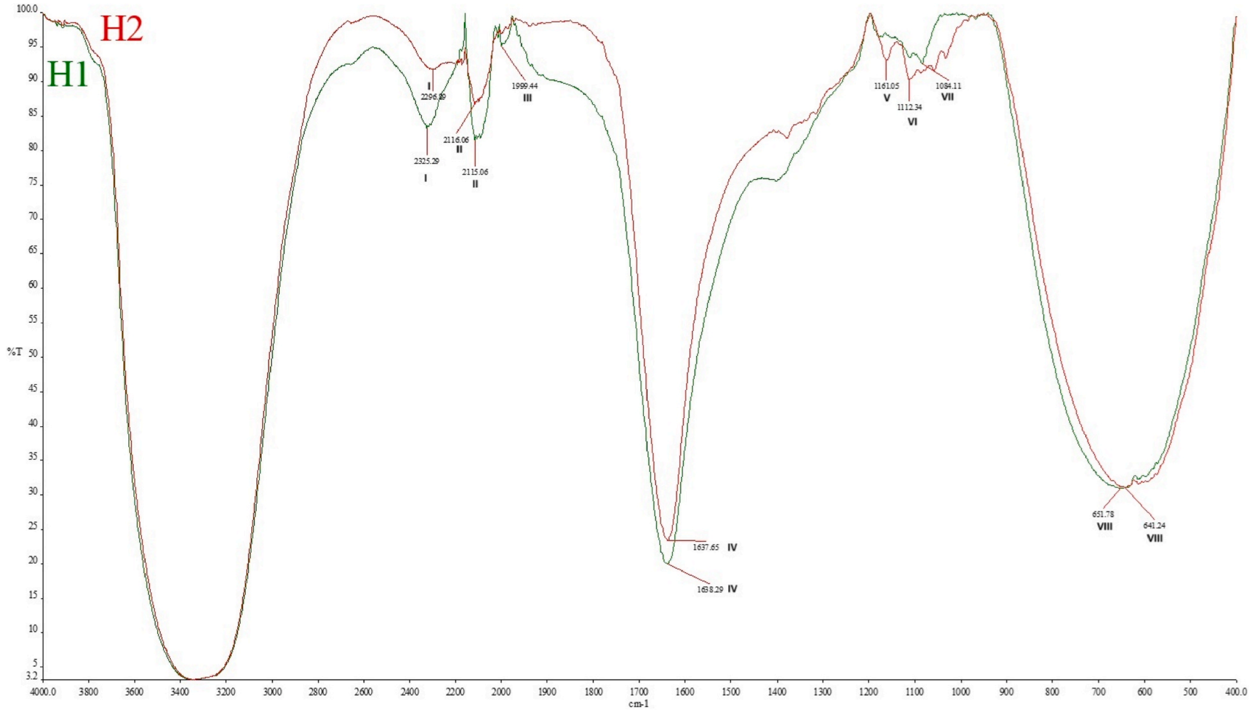

Fig. 3. FTIR- ATR data of *Humulus lupulus* L. aqueous extract (green) and HL-AgNPs (red) [48].

Table 5
The peaks of the FTIR- ATR data (Fig. 3).

	I (cm^{-1})	II (cm^{-1})	III (cm^{-1})	IV (cm^{-1})	V (cm^{-1})	VI (cm^{-1})	VII (cm^{-1})	VIII(cm^{-1})
HL-AgNPs	2296.89	2116.06	–	1637.65	1161.05	1112.34	–	641.24
HL extract	2325.29	2115.06	1999.44	1638.29	–	–	1084.11	651.75

[50]. When incorporating nanoparticles into diesel fuels, it is desirable for them to enhance combustion efficiency by increasing the combustion surface area while minimally affecting other fuel properties. Studies involving nano silver additives have reported an increase in combustion efficiency and in-cylinder pressure values as the combustion surface area expands, often attributed to a micro-explosion phenomenon [51]. Fig. 4 illustrates the effects of different fuels and nano silver additives on the cylinder volume-pressure (P-V) change at an engine power of 4 kW and a constant engine speed of 3000 RPM. The lowest pressure value within

the cylinder, measured at 31.96 bar, was observed for the B_C200 mixture. Conversely, the highest pressure value, measured at 44.62 bar, was recorded for the B_G600 mixture, which included various fuel additives. This data suggests that the addition of nanosilver, particularly when produced using the green synthesis method, increases in-cylinder pressure. The green-synthesized silver nanoparticles (via Humulus lupulus L.) have smaller particle sizes and better dispersion compared to commercial nanoparticles. This promotes more effective catalytic activity during the combustion process, leading to enhanced oxidation of fuel particles and improved energy release within the cylinder. The increased oxidation contributes to higher in-cylinder pressure during the combustion cycle [52]. Furthermore, the increase in the total area on the P-V diagram can be attributed to the inclusion of silver nanoparticles, which positively impacts combustion efficiency [34].

Fig. 5 presents the effects of different fuels and nano silver additives on the change in heat release rate (HRR) with crankshaft angle at an engine load of 4 kW. HRR, calculated from in-cylinder pressure changes in diesel engines, is a critical parameter for understanding the combustion timing within the cylinder [53]. Studies involving nanoparticle additives frequently emphasize their influence on the combustion process in diesel engines [54]. This influence is attributed to the impact of nanoparticles on fuel properties such as viscosity, density, calorific value, and evaporation temperature, as well as their effect on fuel micro-explosions and air/fuel mixture ratios [55]. Research has also indicated that the addition of silver-containing nanoparticles can enhance combustion efficiency [56]. The lowest HRR value, calculated at 31.52 J/^{o}CA, was observed for the B_C200 mixture. Conversely, the highest HRR value, calculated at 41.4 J/^{o}CA, was recorded for the B_G600 mixture. These results indicate that silver nanoparticle additives, particularly those produced through green synthesis, are more effective in increasing combustion efficiency.

Fig. 6 illustrates the variation in CO (carbon monoxide) emissions across different engine powers, fuel mixtures, and nano silver additives. CO emissions indicate incomplete combustion and are typically associated with lean mixtures and oxygen deficiency [57]. Diesel engines, operating at higher lambda values compared to gasoline engines, tend to exhibit lower CO emissions. It's observed that CO emissions decrease as engine power increases. The highest CO emission, measured at 0.41 ppm, occurred at 1 kW engine power for diesel fuel. Numerous studies have indicated that the addition of nanosilver to diesel fuels leads to a significant reduction in CO emissions [58,59]. These studies often attribute this reduction to the increased combustion surface area resulting from mixing nanosilver into the fuel, leading to improved combustion performance and micro-explosions, ultimately resulting in decreased CO emissions. Notably, green nanosilver additives appear to be more effective than industrial nanosilver. This difference may be explained by variations in fuel properties, with green nanosilver potentially forming a better bond with the fuel due to its oxygen content.

When the B_G600 fuel mixture was used at 4 kW engine power, the lowest emission result was obtained at 0.09 ppm. The BD50 mixture, which has a high oxygen concentration because of the biodiesel, had the largest reduction in CO emissions when compared to diesel fuel, reaching 14.28 % at 4 kW engine power. The CO emissions were lowered by 21.42 %, 28.57 %, and 42.85 %, respectively, when 200 ppm, 400 ppm, and 600 ppm of commercial silver nanoparticles were added to 100 % biodiesel in comparison to diesel fuel. On the other hand, CO emissions were decreased by 28.57 %, 64.28 %, and 71.42 %, respectively, when 200 ppm, 400 ppm, and 600 ppm of green synthesis silver nanoparticles were added to 100 % biodiesel. The more oxygen in biodiesel and the higher heating value of the silver nanoparticles added to the fuels are responsible for the drop in CO emissions. Noteworthy is the fact that the improvement in CO emissions at other engine power levels is slightly less pronounced than at 4 kW, but the overall trend aligns with previous studies involving nanosilver mixtures [60,61].

Fig. 7 gives the variation of CO_2 emissions across different engine powers, fuels, and silver nanoparticle additives. CO_2 emissions serve as an indicator of complete combustion [62]. In diesel engines, higher CO2 emissions are typically linked to higher combustion efficiency [63]. However, studies have reported that adding nanosilver to the fuel can increase CO_2 emissions [64,65]. It was understood that the change in CO_2 increased with higher engine power. The highest CO2 emission, reaching 2.59 %, occurred at 4 kW power for the B_G600 mixture, while the lowest was 1.87 % for B_C200 at 2 kW engine power. The BD50 mixture showed the highest

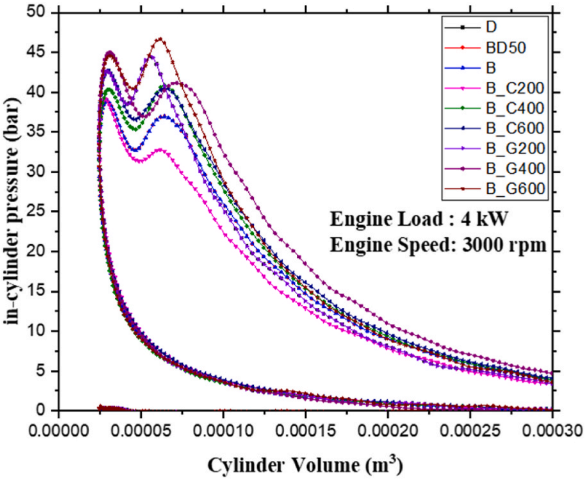

Fig. 4. In-cylinder pressure with cylinder volume for different fuel and nano silver addition.

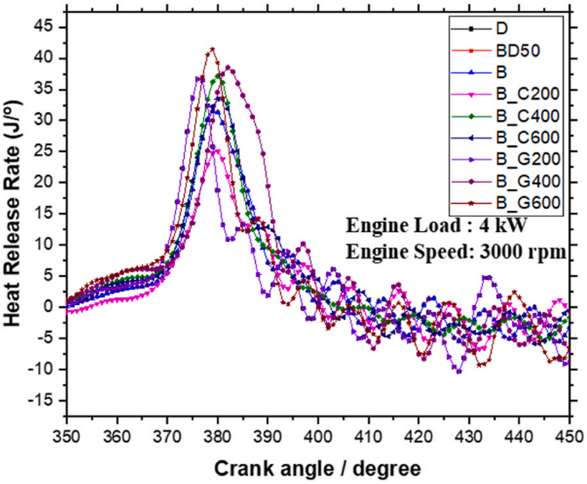

Fig. 5. Heat release rate changing with CAD for different fuel and nano silver addition.

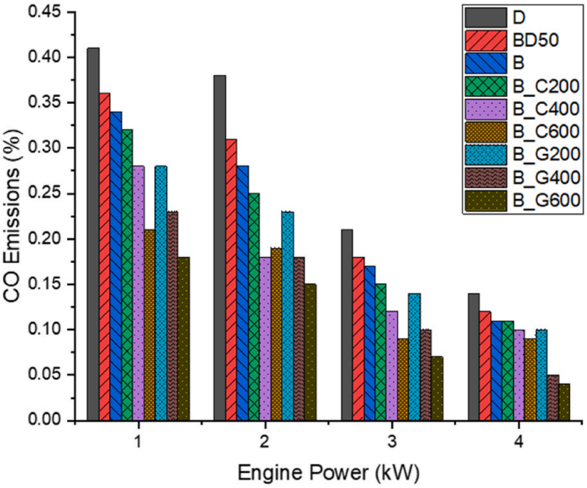

Fig. 6. CO Emission changing with engine power for different fuels and nano silver addition.

increase in CO2 emissions, with a rise of 1.70 % compared to diesel fuel at 4 kW engine power. When adding 200 ppm, 400 ppm, and 600 ppm of commercial silver nanoparticles to 100 % biodiesel compared to diesel fuel, there was an increase of 0.85 %, 2.55 %, and 6.80 %, respectively.

Conversely, when adding 200 ppm, 400 ppm, and 600 ppm of green synthesis silver nanoparticles to 100 % biodiesel, the CO_2 emissions increased by 1.27 %, 2.97 %, and 10.21 %, respectively. CO_2 emissions increase with rising engine power due to the elevated combustion temperature and improved combustion efficiency from adding silver nanoparticles to biodiesel fuel. Notably, the improvement in CO_2 emissions at other engine power levels is slightly less pronounced than at 4 kW, but the overall trend suggests enhanced combustion efficiency. The combined trend of rising CO_2 emissions and decreasing CO emissions points to increased combustion efficiency.

HC emission variation for different engine powers, fuel, and nano silver additives is shown in Fig. 8. HC emission is an indicator of incomplete combustion fuel. It is usually caused by a lack of oxygen in lean mixtures or the inability to decompose fuel fully. Since diesel engines operate at higher lambda values than gasoline engines, lower HC emissions are observed [66]. HC emission decreased with increasing engine power. Nano silver is one of the oxygen-rich additives added to the fuels used in diesel engines. It has been explained in many studies that such fuels are effective in reducing exhaust emission values [67,68]. In these studies, the researchers draw attention to the expansion of the combustion surfaces of fuels by the amount of oxygen in the nanosilvers. The highest HC emission was 212 ppm for diesel fuel at 1 kW engine power. The lowest was 23 ppm for B_G600 at 4 kW engine power. Due to the high oxygen content of biodiesel, D50B50 mixture HC emission decreased 8.88 % compared to diesel fuel. 200 ppm, 400 ppm, and 600 ppm commercial silver nanoparticles added to 100 % biodiesel HC emission decrease 13.33 %, 26.66 % and 35.55 % compared to diesel fuel at 4 kW engine power. On the other hand, 200 ppm, 400 ppm, and 600 ppm green synthesis silver nanoparticles added to 100 %

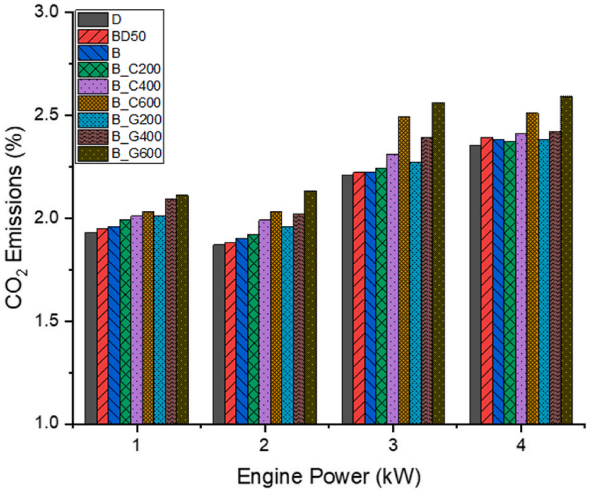

Fig. 7. CO_2 emission changing with engine power for different fuels and nano silver addition.

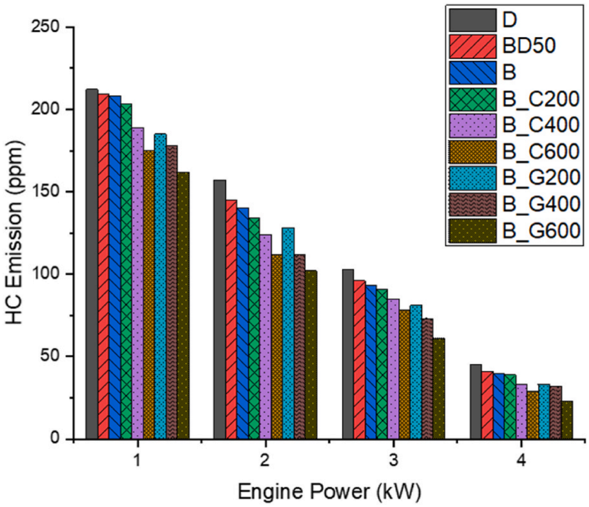

Fig. 8. HC Emission changing with engine power for different fuel and nano silver addition.

biodiesel HC emission decreased 26.66 %, 28.88 %, and 48.88 % compared to diesel fuel at 4 kW engine power. As the engine load increases, HC emissions decrease with the increase in combustion temperature and the effect of fuel oxygen content. The improvement in HC emissions in other engine powers is slightly lower than in 4 kW engine power. The findings obtained showed similarities with other studies in the literature [69].

The exhaust gas temperature variance for varying engine powers, fuels, and nanosilver additions is shown in Fig. 9. Studies have repeatedly demonstrated a strong relationship between exhaust gas temperature and cylinder combustion efficiency. Studies affirming that the addition of nanoparticles to fuels increases combustion efficiency often highlight the impact on combustion surface area, microbursts, and oxygen content [70–72]. Exhaust gas temperature increases with higher engine power. The highest exhaust gas temperature, reaching 583 °C, was recorded at 4 kW for the B_G600 mixture, while the lowest was 225 °C at 1 kW for diesel fuel. The rise in exhaust gas temperature can be attributed to the high combustion temperature of biodiesel, a phenomenon that becomes particularly evident in NO_x emissions. Simultaneously, it can be inferred that combustion efficiency increases due to the decrease in CO emissions and the increase in CO_2 emissions. The BD50 mixture, with its high oxygen content due to biodiesel, exhibited the highest increase in exhaust gas temperature, at 3.59 %, at 4 kW engine power. When adding 200 ppm, 400 ppm, and 600 ppm of commercial silver nanoparticles to 100 % biodiesel compared to diesel fuel, there was an increase in exhaust gas temperature by 4.53 %, 6.04 %, and 7.93 %, respectively. Furthermore, when incorporating 200 ppm, 400 ppm, and 600 ppm of green synthesis silver nanoparticles into 100 % biodiesel compared to diesel fuel, exhaust gas temperature increased by 6.23 %, 1.51 %, and 10.20 %, respectively. Because of the higher combustion temperature, the exhaust gas temperature rises with increased engine load. At other engine power levels, there were increases in exhaust gas temperature, albeit at similar values.

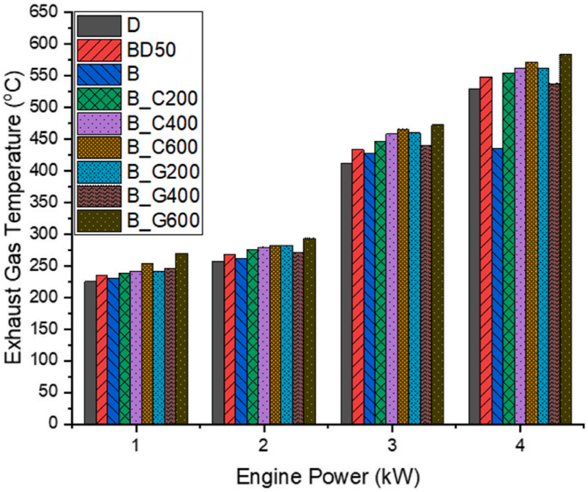

Fig. 9. Exhaust gas temperature changing with different engine power, fuels, and nano silver addition.

Fig. 10 illustrates the variation in NO_x emissions for different engine powers, fuels, and nano silver additives. Generally, there was an observed increase in NO_x emissions with the rise in power, a trend often observed in diesel engines. NO_x emissions in diesel engines are primarily a result of increased end-of-combustion temperature [73]. These temperature values can vary depending on combustion efficiency and the air-to-fuel ratio within the cylinder. Studies examining the effects of nanosilver addition to fuels have noted an increase in NO_x emissions, attributing this phenomenon to the expanded combustion surfaces of the fuels and the oxygen content in the nanoparticles [74,75]. At 2 kW engine power, the lowest NOx emission recorded was 91 ppm for B_C200, while the highest was 237 ppm at 4 kW for B_G400. The addition of biodiesel was associated with an increase in NO_x emissions, with the lowest NO_x emission observed for B_C200 and the highest for B_G400 at engine powers other than 1 kW. Notably, the BD50 mixture exhibited the highest increase in NO_x emissions, rising by 9.08 % at 1 kW engine power. For 100 % biodiesel, an expected increase in NO_x emissions of approximately 18.16 % was observed. Adding 200 ppm of commercial silver nanoparticles to 100 % biodiesel resulted in a 12.09 % improvement compared to diesel fuel at 4 kW engine power. However, the addition of 400 ppm of commercial silver nanoparticles caused a 4.18 % deterioration, and adding 600 ppm resulted in a 1.86 % deterioration. When evaluating silver nanoparticles produced and added via the green synthesis method, an improvement of 7.44 % was achieved by adding 200 ppm green synthesis silver nanoparticles to 100 % biodiesel compared to diesel fuel at 4 kW engine power. However, adding 400 ppm of green synthesis silver nanoparticles led to a deterioration of 7.4 %, and adding 600 ppm resulted in a 5.11 % deterioration. As engine load increased, the improvements diminished due to the rise in combustion temperature. Additionally, NO_x emissions decreased with the addition of 200 ppm silver nanoparticles but increased with more silver nanoparticles addition.

Fig. 11 illustrates the variability in soot emissions across various engine powers, fuel types, and the inclusion of nano silver additions. A decrease in soot emission change was found with an increase in engine power. Diesel fuel exhibited the highest soot emissions across all engine powers. For example, at 1 kW, soot emissions were 12.5 %, and at 4 kW, they were 7.8 %. These higher values are consistent with the incomplete combustion of diesel due to its lack of oxygen content. Soot emissions were lower for biodiesel compared to diesel. For instance, at 1 kW, biodiesel showed 12.0 % emissions compared to 12.5 % for diesel, and at 4 kW, emissions dropped to 7.5 %. This reduction is attributed to the higher oxygen content of biodiesel, which facilitates more complete combustion and reduces soot formation. The 50 % diesel-50 % biodiesel blend (BD50) resulted in slightly lower soot emissions compared to pure diesel but higher emissions than pure biodiesel. For instance, at 1 kW, BD50 recorded 12.3 %, compared to 12.5 % for diesel and 12.0 % for biodiesel. This trend is expected as blending diesel with biodiesel introduces oxygenated fuel properties, improving combustion efficiency. Adding commercial silver nanoparticles to biodiesel significantly reduced soot emissions across all engine powers. For example, at 1 kW, B_C200, B_C400, and B_C600 recorded emissions of 11.6 %, 11.1 %, and 10.5 %, respectively, compared to 12.0 % for pure biodiesel.

This reduction is attributed to the catalytic effect of silver nanoparticles, which enhance fuel atomization and promote more complete combustion, thereby reducing soot formation. Green-synthesized nanoparticles outperformed commercial nanoparticles in reducing soot emissions. For instance, at 1 kW, B_G200, B_G400, and B_G600 showed emissions of 11.3 %, 10.7 %, and 10.1 %, respectively. Similarly, at 4 kW, B_G600 achieved the lowest emission level of 6.0 %, compared to 7.2 % for B_C200 and 7.5 % for pure biodiesel. The superior performance of green-synthesized nanoparticles is likely due to their smaller particle size and better dispersion, which enhance the catalytic activity and further reduce soot. Soot emissions decreased with increasing engine power across all fuel blends. This trend is due to improved combustion conditions at higher engine powers, which reduce incomplete combustion and soot formation. At 4 kW, the lowest soot emissions were recorded for B_G600 (6.0 %), followed by B_G400 (6.2 %) and B_C600 (6.3 %). Pure diesel and BD50 had the highest emissions at 7.8 % and 7.7 %, respectively.

The catalytic properties of silver nanoparticles promote better oxidation of hydrocarbons during combustion, leading to reduced soot emissions. The presence of green-synthesized nanoparticles further improves combustion efficiency due to their enhanced

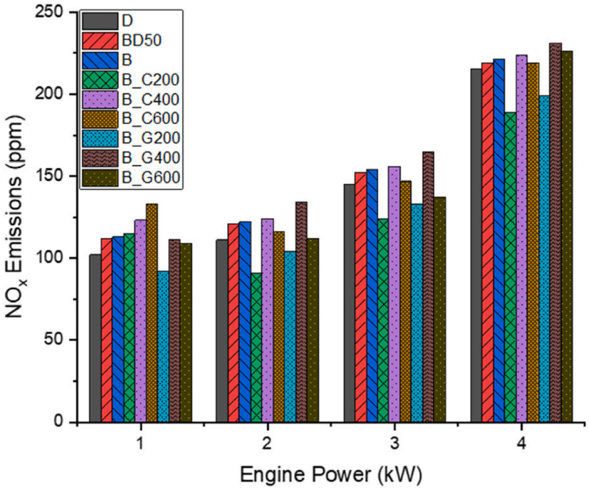

Fig. 10. NO_x Emission variation with engine power for different fuels and nano silver additions.

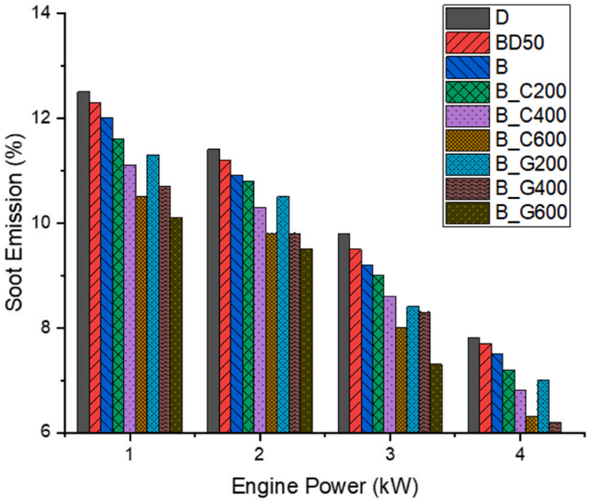

Fig. 11. Soot Emissions changing with engine power for different fuels and nano silver addition.

dispersion and higher catalytic activity compared to commercial nanoparticles [76]. Biodiesel's inherent oxygen content contributes to lower soot emissions compared to diesel. This effect is amplified when nanoparticles are added, as they enhance the breakdown of hydrocarbons and reduce soot precursors. Increasing the nanoparticle concentration (from 200 ppm to 600 ppm) consistently reduced soot emissions. This highlights the effectiveness of higher concentrations in achieving better combustion and lower soot formation.

Fig. 12 illustrates the variation in BSFC across varied engine powers, fuel types, and the inclusion of nanosilver additives. The term "BSFC" refers to measuring fuel consumption relative to the amount of power generated. The data indicated a negative correlation between the BSFC change and the engine power rise. Numerous prior investigations have elucidated that an augmentation in the quantity of BSFC may arise due to the low thermal efficiency of biodiesel and its elevated viscosity and density values [77]. However, although the inclusion of nanosilver in biodiesel increases viscosity and density measurements, the observed reduction in BSFC is unanticipated. The phenomenon of partial healing of the burn can elucidate the present scenario. Studies undertaken on incorporating qualitative nanoparticles have yielded comparable findings, as stated. The researchers in this study noted that the microburst phenomenon has a partly enhancing effect on combustion, mostly attributed to its ability to increase the combustion surface [78–80]. The BD50 combination had the greatest BSFC at a measured value of 1135 g/kWh and an engine power of 1 kW. The B_G600 achieved the lowest BSFC of 553 g/kWh at an engine power of 4 kW. The D50B50 mixture had the biggest increase in BSFC at an engine power of 4 kW, with a notable rise of 4.17 %. This can be attributed to the relatively low calorific value of biodiesel. The introduction of commercial silver nanoparticles at concentrations of 200 ppm, 400 ppm, and 600 ppm into 100 % biodiesel resulted in enhancements of 1.66 %, 3.33 %, and 6.01 % in BSFC, respectively, as compared to conventional diesel fuel at a 4 kW engine power condition. The addition of green synthesis silver nanoparticles at concentrations of 200 ppm, 400 ppm, and 600 ppm to 100 % biodiesel resulted in improvements of 4.17 %, 6.01 %, and 7.67 % in BSFC, respectively, as compared to diesel fuel under an engine power of 4 kW. An

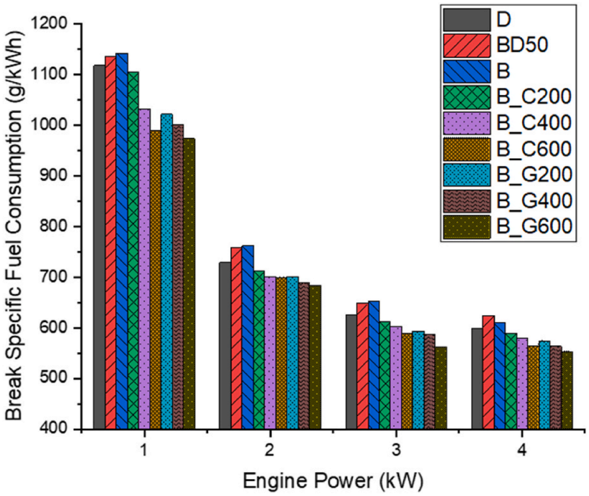

Fig. 12. BSFC changing with engine power for different fuels and nano silver addition.

anticipated consequence of biodiesel's relatively low calorific value is a predicted rise in BSFC. The incorporation of silver nanoparticles is anticipated to enhance the BSFC, mostly attributed to the augmentation of the heating value. The incorporation of silver nanoparticles generated by the green synthesis technique resulted in an additional enhancement.

Fig. 13 illustrates the variations in thermal efficiency across varied engine powers, fuel types, and the use of nano silver. Pure diesel (D) exhibited the highest thermal efficiency at all engine power levels compared to pure biodiesel (B) and biodiesel blends. For instance, at 4 kW, diesel achieved 25.51 %, whereas biodiesel achieved 23.5 %. The decrease in thermal efficiency for biodiesel is attributed to its lower calorific value and higher viscosity compared to diesel, which negatively impacts fuel atomization and combustion. The thermal efficiency of BD50 was consistently lower than pure diesel but higher than pure biodiesel (B) at all engine power levels. For example, at 2 kW, BD50 achieved 19.48 %, compared to 20.96 % for diesel and 19.3 % for biodiesel. This indicates that blending diesel and biodiesel helps mitigate the efficiency loss associated with biodiesel's properties while maintaining some of its environmental benefits. The addition of commercial silver nanoparticles to biodiesel increased thermal efficiency across all engine powers compared to pure biodiesel. For instance, at 4 kW, B_C200, B_C400, and B_C600 achieved efficiencies of 24.26 %, 24.81 %, and 25.71 %, respectively, compared to 23.5 % for pure biodiesel. The improvement is attributed to the catalytic effects of silver nanoparticles, which enhance combustion efficiency by promoting better oxidation of the fuel. Blends with green-synthesized silver nanoparticles exhibited higher thermal efficiency than those with commercial nanoparticles. For example, at 4 kW, B_G200, B_G400, and B_G600 achieved efficiencies of 25.02 %, 25.51 %, and 26.17 %, respectively, surpassing their commercial counterparts. The superior performance of green-synthesized nanoparticles is likely due to their smaller particle size and better dispersion in biodiesel, which enhances their catalytic activity and fuel-air mixing during combustion. Across all fuel blends, thermal efficiency increased with engine power, peaking at 4 kW. This is expected, as higher engine power typically corresponds to improved combustion conditions and

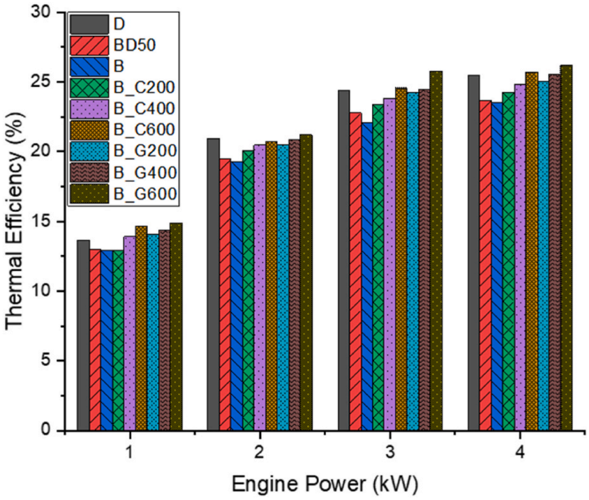

Fig. 13. Thermal efficiency changing with engine power for different fuels and nano silver addition.

reduced relative heat losses. At 4 kW, the highest thermal efficiency was observed for B_G600 (26.17 %), followed by diesel (25.51 %) and B_C600 (25.71 %).

Increasing the concentration of nanoparticles (from 200 ppm to 600 ppm) consistently improved thermal efficiency, regardless of the synthesis method. This suggests that higher concentrations enhance the catalytic effect, leading to better combustion performance. Green-synthesized silver nanoparticles outperformed commercial ones across all power levels and concentrations, highlighting the potential of green synthesis methods for superior biodiesel enhancement [81–85]. While the use of nanoparticles improves thermal efficiency, associated emissions (e.g., NOx) may increase due to higher combustion temperatures. Further studies are needed to optimize nanoparticle concentrations to balance performance and environmental impacts [86–88].

Diesel achieved the highest baseline thermal efficiency, while biodiesel blends showed improvements with silver nanoparticle additives. Green-synthesized nanoparticles outperformed commercial nanoparticles, with B_G600 achieving the highest thermal efficiency (26.17 %) at 4 kW. Increasing engine power and nanoparticle concentration positively impacted thermal efficiency, showcasing the catalytic potential of silver nanoparticles in biodiesel fuels.

4. Conclusions

This study demonstrates that the addition of silver nanoparticles to biodiesel significantly influences diesel engine performance and emission characteristics. Silver nanoparticles, synthesized through a green method using *Humulus lupulus* L., and commercially available silver nanoparticles were investigated for their effects on biodiesel blends compared to diesel fuel under partial load conditions (1–4 kW). The findings reveal that green-synthesized nanoparticles consistently outperform commercial nanoparticles in enhancing combustion efficiency and reducing harmful emissions.

- The inclusion of silver nanoparticles, particularly green-synthesized ones, improved in-cylinder pressure and heat release rates, with the maximum pressure reaching 44.62 bar for B_G600 at 4 kW.
- Thermal efficiency increased with nanoparticle addition, reversing the decline observed when biodiesel was blended with diesel. Green-synthesized nanoparticles showed greater efficiency improvements than commercial ones.
- The addition of biodiesel to diesel fuel increased brake-specific fuel consumption (BSFC), a result of biodiesel's lower energy content.
- Silver nanoparticle additives reduced BSFC, with green-synthesized nanoparticles demonstrating a substantial reduction, achieving 7.67 % improvement at 600 ppm compared to diesel fuel.
- CO emissions decreased significantly with nanoparticle addition, with a reduction of up to 71.42 % for B_G600 at 4 kW, owing to the higher oxygen content of biodiesel and improved combustion.
- HC emissions were reduced by 48.88 % with B_G600 at 4 kW, indicating better fuel oxidation and combustion completeness.
- A substantial decline in particulate emissions was observed, with green-synthesized nanoparticles offering superior reductions compared to commercial ones.
- Improved combustion efficiency led to increased CO_2 emissions, with a peak of 2.59 % for B_G600 at 4 kW.
- NO_x emissions increased with biodiesel and further with nanoparticle addition, reaching a peak of 237 ppm for B_G400 at 4 kW, due to elevated combustion temperatures.
- Exhaust gas temperature rose with biodiesel and further increased with nanoparticle addition, peaking at 583 °C for B_G600, reflecting enhanced combustion efficiency.

The results emphasize the potential of green-synthesized silver nanoparticles as a sustainable and effective additive for biodiesel. While these nanoparticles significantly reduce CO, HC, and particulate emissions and improve combustion efficiency, the associated increases in NO_x and CO_2 emissions highlight a trade-off that warrants further optimization. Future research should focus on balancing these outcomes by exploring additional additives, varying engine operating conditions, and scaling this technology for broader use. This study underscores the importance of green nanotechnology in advancing biodiesel as a viable alternative fuel, offering a pathway toward more sustainable and efficient energy solutions for diesel engines.

CRediT authorship contribution statement

Usame Demir: Writing – review & editing, Writing – original draft, Methodology, Formal analysis, Conceptualization. **Merve Keskin:** Writing – original draft, Resources, Investigation, Formal analysis. **Salih Özer:** Visualization, Validation, Methodology, Investigation, Data curation. **Gokhan Coskun:** Writing – review & editing, Writing – original draft, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

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