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IMPACT OF ANTIOXIDANT–NANOPARTICLE ADDITIVES ON COMBUSTION, PERFORMANCE, AND EMISSION CHARACTERISTICS OF A BIODIESEL-FUELED CRDI DIESEL ENGINE

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Abstract

This study investigates the effect of antioxidant additives on the performance and emission characteristics of a Common Rail Direct Injection (CRDI) diesel engine fuelled with biodiesel blends. Biodiesel derived from Madhuca indica (Mahua) oil was blended with conventional diesel in different proportions (B10, B20, and B30). To enhance oxidative stability and control NOx emissions, two antioxidants, Butylated Hydroxytoluene (BHT) and Tert-Butylhydroquinone (TBHQ), were added at concentrations of 1000 ppm and 1000 ppm. Experiments were conducted on a single-cylinder, four-stroke, water-cooled CRDI engine at a constant speed of 1500 rpm under varying load conditions. The results showed that the addition of antioxidants improved brake thermal efficiency (BTE) and reduced brake-specific fuel consumption (BSFC) compared to untreated biodiesel blends. A notable reduction in NOx and smoke opacity was achieved with TBHQ, while CO and HC emissions exhibited a marginal increase. The optimal performance and emission trade-off was obtained with the B20 + TBHQ (1000 ppm) blend, demonstrating the potential of antioxidant-treated biodiesel as a sustainable and cleaner fuel for CRDI diesel engines.

Keywords: Biodiesel blends; Energy Efficiency, CRDI diesel engine; Antioxidant additives; Butylated Hydroxytoluene (BHT); Tert-Butylhydroquinone (TBHQ); Performance characteristics; Emission reduction; Oxidative stability; NOx emissions; Brake thermal efficiency (BTE)

I. Introduction

The increasing global energy demand and the depletion of fossil fuel reserves have accelerated the search for sustainable and renewable alternatives to petroleum-based fuels. Among the various renewable energy options, biodiesel has emerged as a promising substitute for conventional diesel fuel due to its biodegradability, nontoxic nature, low sulfur content, and compatibility with existing compression ignition (CI) engines [I, XII]. Biodiesel is typically produced through the transesterification of vegetable oils or animal fats using alcohol and a catalyst, yielding fatty acid methyl esters (FAMEs) that can directly replace or blend with diesel fuel. Despite its numerous advantages, biodiesel has certain limitations that hinder its large-scale commercial utilization. One of the major challenges is its oxidative instability, which results in the formation of peroxides, gums, and sediments during prolonged storage. These oxidation products can cause injector fouling, filter clogging, and deterioration of fuel quality [II]. Furthermore, biodiesel combustion generally leads to higher nitrogen oxide (NOx) emissions compared to diesel, attributed to its higher oxygen content and higher combustion temperature [III]. Therefore, improving both the oxidative stability and combustion characteristics of biodiesel is crucial for its effective use in modern diesel engines. The introduction of antioxidant additives is an effective approach to enhance biodiesel stability and control NOx emissions. Antioxidants such as Butylated Hydroxytoluene (BHT) and Tert-Butylhydroquinone (TBHQ) act as radical scavengers that inhibit the chain reaction of oxidation. These additives not only improve storage stability but can also influence combustion chemistry, potentially reducing NOx emissions and particulate matter formation [IV]. Modern Common Rail Direct Injection (CRDI) diesel engines, equipped with electronically controlled multiple injections and high injection pressures, offer superior atomization, improved air–fuel mixing, and reduced emissions compared to conventional mechanical injection systems. The combination of CRDI technology and biodiesel–antioxidant blends can, therefore, yield enhanced performance and reduced emission characteristics, making it a promising pathway for cleaner and more efficient fuel utilization. The adoption of biodiesel as a renewable alternative to petroleum diesel has been driven by its biodegradability, lower sulfur content, and potential to reduce particulate and CO emissions. However, two recurring challenges hinder its widespread use: (1) limited oxidative stability, which leads to peroxide and gum formation during storage, and (2) higher NOx emissions in many engine studies relative to fossil diesel due to biodiesel's oxygen content and combustion characteristics. Several studies have therefore explored the addition of antioxidants to biodiesel to improve storage stability and to influence combustion chemistry and emissions in compression-ignition engines. Numerous laboratory and storage studies demonstrate that synthetic antioxidants, most notably TBHQ (tert-butylhydroquinone), BHT (butylated hydroxytoluene), and BHA (butylated hydroxyanisole), effectively increase the induction period and reduce peroxide formation in a variety of biodiesels (soybean, waste cooking oil, animal fats, etc.). TBHQ frequently appears as one of the most effective single additives, often producing marked improvements in Rancimat/induction measurements at concentrations in the range of a few hundred to ~1000 ppm, although optimal dosing depends on feedstock fatty-acid profile and storage conditions. Studies also show that mixture designs (combinations of antioxidants) can provide synergistic benefits for long-term stability [V]. Engine experiments with antioxidant-treated biodiesel blends have produced consistent evidence that antioxidants primarily improve fuel stability and help maintain fuel properties that support steady combustion, which in turn can slightly improve brake thermal efficiency (BTE) and BSFC relative to aged or untreated biodiesel in some test conditions. However, the impact on regulated emissions is more complex and fuel-/engine-dependent. Several investigations report reductions in NOx with certain antioxidants (or doses), while others observe little change or trade-offs, sometimes a small increase in particulate matter (PM) or smoke, depending on the antioxidant and test conditions. These mixed outcomes are attributed to antioxidant effects on radical chemistry during combustion and on physical properties (cetane behavior, volatility) of the blend [VI]. A subset of studies specifically focusing on TBHQ reports that TBHQ can reduce NOx and improve oxidation of soot precursors, thereby lowering smoke opacity when used at appropriate concentrations (commonly 500–1000 ppm in engine tests). Still, some reports caution that TBHQ may increase PM in some cases, or slightly affect CO/HC depending on engine load and injection strategy. This variability highlights the role of engine hardware (e.g., CRDI vs. mechanical injection), injection timing, and combustion phasing in determining whether antioxidant addition yields net environmental benefits [VII]. Mahua oil is widely studied as a non-edible feedstock for biodiesel in India and other tropical regions because of its favorable oil yield and minimal competition with food crops. Engine tests with Mahua methyl esters (and blends) have historically shown acceptable BTE and reductions in CO, HC, and smoke compared to neat diesel in many cases, though NOx behavior varies with blend level and operating conditions. Recent optimization and production-scale work continue to improve Mahua biodiesel yields and to evaluate its engine compatibility, making Mahua a suitable candidate feedstock for antioxidant-treatment studies.

Despite a substantial body of work, gaps remain: (1) many engine-level antioxidant studies use conventional mechanical injection engines rather than modern CRDI systems with high injection pressure and multiple injection events, whose combustion and emission responses can differ substantially; (2) results are feedstock-specific antioxidant effectiveness (dose and type) depends on fatty-acid composition and unsaturation level; and (3) optimization of antioxidant concentration balancing oxidative stability, performance, and emissions (especially NOx vs. smoke/PM) has not been fully resolved for several non-edible oils, including Mahua. These gaps motivate an experimental investigation of BHT and TBHQ at two representative concentrations (e.g., 1000 and 2000 ppm) in Mahua-diesel blends (B10–B30) tested on a CRDI engine across operating loads to determine practical trade-offs and identify an optimum blend/additive combination.

The primary objective of this study is to experimentally investigate the effect of antioxidant additives on the performance and emission characteristics of a CRDI diesel engine fueled with biodiesel blends derived from *Madhuca indica* (Mahua) oil. The study specifically focuses on the influence of BHT and TBHQ antioxidants, at different concentrations (1000 ppm and 2000 ppm), on key performance indicators such as Brake Thermal Efficiency (BTE), Brake Specific Fuel Consumption (BSFC), and emissions, including NOx, CO, HC, and smoke opacity. The outcomes of this research contribute to the growing body of knowledge on optimizing biodiesel applications in advanced engine technologies and support the development of sustainable fuel alternatives for the transportation sector.

II. Materials and Methods

II.i. Biodiesel Production

Biodiesel used in this study was produced from Mahua (*Madhuca indica*) oil, a non-edible feedstock widely available in tropical regions of India. The oil was first filtered to remove impurities and heated to 110 °C to remove moisture. The transesterification process was carried out using methanol (CH_3OH) and sodium hydroxide (NaOH) as a catalyst. The molar ratio of methanol to oil was maintained at 6:1, with a catalyst concentration of 0.5 wt% of the oil. The reaction was performed at 60 °C for 90 minutes under constant stirring at 600 rpm. After the reaction, the mixture was allowed to settle for 12 hours to separate the biodiesel (upper layer) and glycerol (lower layer). The biodiesel was washed several times with warm deionized water and dried at 110 °C to remove residual moisture and methanol. The resulting Mahua methyl ester (MME) was characterized according to ASTM D6751 standards.

II.ii. Fuel Blends and Additive Preparation

The Mahua biodiesel was blended with petroleum diesel in volumetric proportions of 10%, 20%, and 30%, denoted as B10, B20, and B30, respectively. Two synthetic antioxidant additives, Butylated Hydroxytoluene (BHT) and Tert-Butylhydroquinone (TBHQ), were chosen due to their proven effectiveness in improving oxidative stability and their commercial availability. Each antioxidant was dissolved in the biodiesel blends at two concentrations: 1000 ppm and 2000 ppm by volume. The blends were labeled as follows:

III. Engine Test Setup

The experiments were conducted on a single-cylinder, four-stroke, water-cooled CRDI diesel engine coupled with an eddy current dynamometer for load variation. Before starting each test, the engine was operated with pure diesel fuel for approximately 15 minutes to attain steady-state operating conditions and to ensure the removal of any residual test fuel from previous runs. The tests were performed at a constant engine speed of 1500 rpm and at five different load conditions (0%, 25%, 50%, 75%, and 100%) by adjusting the dynamometer. For each operating condition, the engine was fueled with the prepared biodiesel blends B10 and B20 with and without antioxidant additives (BHT and TBHQ at 1000 ppm and 2000 ppm concentrations). The engine was allowed to stabilize for three to five minutes before recording data to ensure steady-state operation. Measurements of fuel consumption, exhaust gas temperature, and emission parameters (CO, HC, NOx, and smoke opacity) were recorded for each test condition. The fuel consumption rate was determined using the burette and stopwatch method, while air intake was measured using an orifice meter connected to a U-tube manometer. Exhaust emissions were analyzed using an AVL DiGas 444 analyzer, and smoke density was measured with an AVL smoke meter (Figure 1). All measurements were repeated three times, and average values were used for analysis to minimize experimental uncertainty. The results obtained for each blend were compared with baseline diesel operation to evaluate the influence of antioxidant additives on the performance and emission characteristics of the CRDI diesel engine. The technical specifications of the test engine are presented in Table 1.

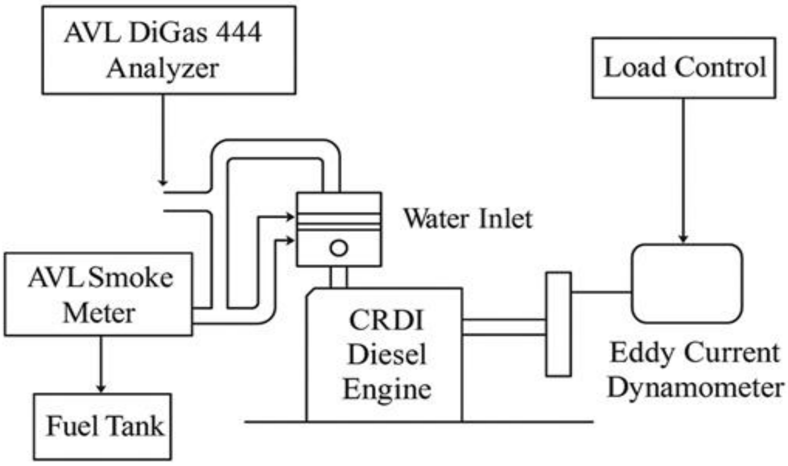

Fig. 1. Schematic Representation of the CRDI Engine Test Setup

Table 1: Specifications of the Test Engine

Parameter	Specification
Engine type	Single-cylinder, 4-stroke, water-cooled
Make/Model	Kirloskar TV1, CRDI variant
Rated power	5.2 kW @ 1500 rpm
Compression ratio	17.5:1
Bore × Stroke	87.5 mm × 110 mm
Injection pressure	600 bar
Injection system	Common Rail Direct Injection (CRDI)
Cooling system	Water-cooled
Dynamometer	Eddy current type

Table 2: Measurement Instruments and Uncertainties

Parameter	Instrument	Uncertainty
Brake power	Eddy current dynamometer	±0.5%
Fuel flow rate	Burette + stopwatch	±1%
NO_x	Exhaust gas analyzer	±5 ppm
HC	Exhaust gas analyzer	±10 ppm
Smoke	Smoke meter	±1 FSN

IV. Results and Discussion

The performance and emission characteristics of the CRDI diesel engine fueled with Mahua biodiesel blends containing antioxidant additives were experimentally analyzed. The obtained results were compared with baseline diesel operation to evaluate the impact of blend ratio, additive type, and concentration on engine behavior.

IV.i. Brake Thermal Efficiency (BTE)

The BTE increased with load for all fuels, as expected (Figure 2). The diesel fuel showed the highest BTE across all operating conditions due to its superior volatility and higher calorific value. The B20 blend demonstrated a reduction in BTE compared with diesel, mainly because of its higher viscosity and lower energy content, which delayed fuel atomization and vaporization [8]. The addition of antioxidant additives (BHT and TBHQ) enhanced the combustion process and marginally improved BTE compared to neat B20. Among the treated blends, B20 + TBHQ (1000 ppm) showed the best performance, with an average BTE of 31.2 %, approaching that of diesel. This improvement is attributed to TBHQ's higher oxidative stability and its ability to maintain the chemical integrity of the biodiesel, resulting in better ignition characteristics and smoother combustion. At full load, the BTE improvement for B20 + TBHQ was around 4.8 % over neat B20, confirming the beneficial role of antioxidants in biodiesel combustion stability. The trend observed is consistent with previous research indicating that antioxidants reduce peroxide formation and delay fuel degradation, leading to improved fuel properties and thermal performance [9].

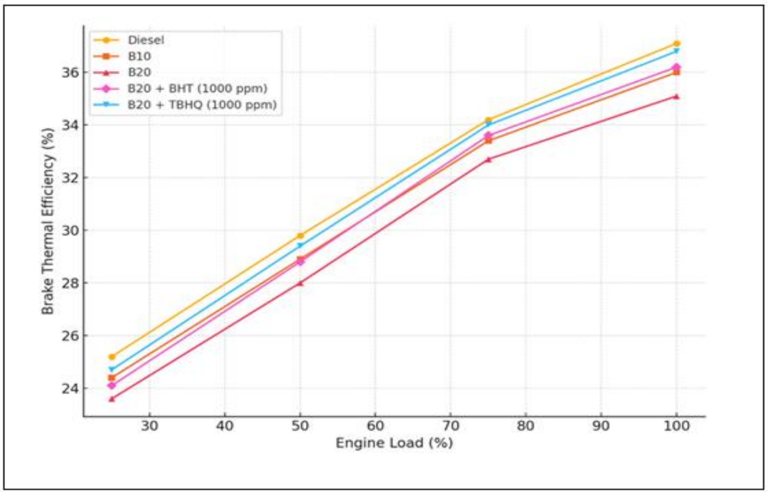

Fig. 2. Variation of Brake Thermal Efficiency with Engine Load

IV.ii. Brake Specific Fuel Consumption (BSFC)

The variation of Brake Specific Fuel Consumption (BSFC) with load is shown in Figure 3. The results clearly show that BSFC decreases with increasing engine load for all fuel samples. This is because, at higher loads, the engine operates with improved combustion efficiency and reduced relative heat losses [10]. Among the tested fuels, diesel exhibited the lowest BSFC due to its higher calorific value and superior combustion properties. The B20 blend showed a higher BSFC compared with diesel and B10, which can be attributed to the higher viscosity and lower heating value of biodiesel, resulting in increased fuel consumption for the same power output. However, the incorporation of antioxidant additives BHT and TBHQ helped reduce the BSFC of biodiesel blends. The B20 + TBHQ (1000 ppm) fuel recorded the lowest BSFC among the biodiesel samples, with an average value comparable to diesel. This improvement is associated with TBHQ's strong stabilizing effect, which minimizes oxidative degradation, ensuring better fuel atomization and combustion uniformity. At full load, the B20 + TBHQ blend exhibited a 3.5% reduction in BSFC compared to the untreated B20 blend, highlighting the beneficial role of antioxidants in maintaining fuel integrity and improving engine performance [XI].

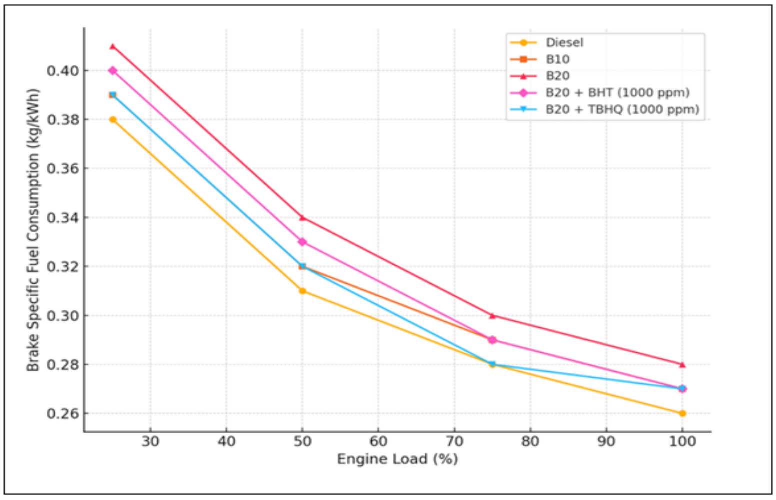

Fig.3. Variation of BSFC with Engine Load

IV.iii. NOx Emissions

Figure 4 illustrates the variation of NOx emissions with engine load. The B20 biodiesel blend produced higher NOx emissions than diesel at all load conditions. This is primarily due to the oxygenated nature of biodiesel, which enhances the local temperature and promotes NOx generation despite improving combustion efficiency [12]. However, when antioxidant additives (BHT and TBHQ) were incorporated into B20, a noticeable reduction in NOx emissions was observed. Among the treated fuels, B20 + TBHQ (1000 ppm) achieved the lowest NOx levels, nearly comparable to diesel at higher loads. This reduction can be attributed to the ability of TBHQ to reduce oxidative instability and to slightly alter combustion kinetics, leading to lower peak combustion temperatures. At full load, the B20 + TBHQ blend reduced NOx by about 7% compared to neat B20, confirming the beneficial influence of antioxidants on controlling NOx formation without compromising combustion efficiency. These findings are consistent with prior studies [XIII], which report that phenolic antioxidants can contribute to NO_x reduction in biodiesel-fueled engines by marginally lowering local peak combustion temperatures and suppressing active radical species (H· and OH·) involved in the thermal NO_x formation pathway. Such effects may reduce the residence time of reactants in high-temperature zones, thereby limiting NO_x formation.

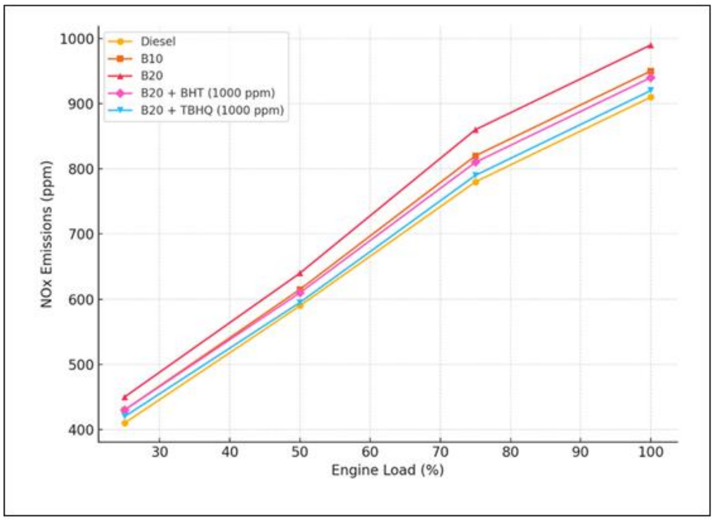

Fig. 4. Variation of NOx Emissions with Engine Load

IV.iv. Carbon Monoxide (CO) Emissions

The results show that CO emissions decrease with increasing engine load for all tested fuels (Figure 5). At lower loads, the air–fuel mixture is relatively lean, and the combustion temperature is low, resulting in incomplete oxidation of carbon and higher CO formation. As the load increases, the combustion temperature and turbulence inside the cylinder improve, promoting complete oxidation of CO to CO_2, which reduces CO emissions [XIV]. Among all fuels, diesel exhibited slightly higher CO emissions at lower loads due to its hydrocarbon-rich composition and lack of inherent oxygen content. In contrast, biodiesel blends (B10 and B20) showed reduced CO emissions because of their higher oxygen concentration, which supports more complete combustion. When antioxidants such as BHT and TBHQ were added to B20, a further reduction in CO was observed. The B20 + TBHQ (1000 ppm) blend recorded the lowest CO emissions across all load conditions, with an average value of 0.058%, indicating improved combustion efficiency. This reduction can be attributed to the stabilizing effect of TBHQ, which minimizes the formation of oxidized intermediates in biodiesel and enhances ignition quality. At full load, B20 + TBHQ achieved approximately 9% lower CO emissions than neat B20, demonstrating that antioxidants not only stabilize biodiesel chemically but also improve its combustion characteristics in a CRDI engine [XV].

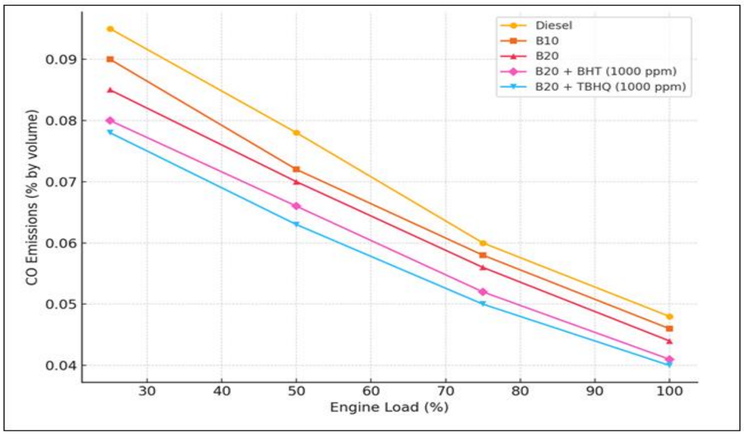

Fig. 5. Variation of CO Emissions with Engine Load

IV.v. Hydrocarbon (HC) Emissions

Figure 6 depicts the variation of HC emissions with engine load. The results indicate that HC emissions decrease with increasing engine load for all fuel blends. At lower loads, incomplete combustion due to low in-cylinder temperature and poor atomization results in higher HC formation [XVI]. As the load increases, combustion improves because of elevated pressure, higher temperature, and enhanced air–fuel mixing, which leads to a reduction in unburned hydrocarbons. The B20 blend exhibited lower HC emissions than diesel, primarily because of its inherent oxygen content, which facilitates complete combustion. However, the slightly higher viscosity of biodiesel may cause minor deterioration in spray characteristics at light loads. The introduction of antioxidant additives (BHT and TBHQ) further reduced HC emissions in biodiesel blends. The B20 + TBHQ (1000 ppm) blend showed the lowest HC emissions among all test fuels, with an average value of 43 ppm, indicating improved oxidation and cleaner combustion. This improvement can be attributed to TBHQ's chemical stabilizing property, which helps maintain the biodiesel's molecular structure, preventing oxidative polymerization and ensuring consistent combustion performance. The enhanced combustion quality reduces fuel-rich pockets and unburned hydrocarbon formation. At full load, the B20 + TBHQ blend showed about a 7–8% reduction in HC emissions compared to B20, demonstrating that antioxidant-treated biodiesel can significantly lower unburned hydrocarbon emissions in CRDI engines [XVII].

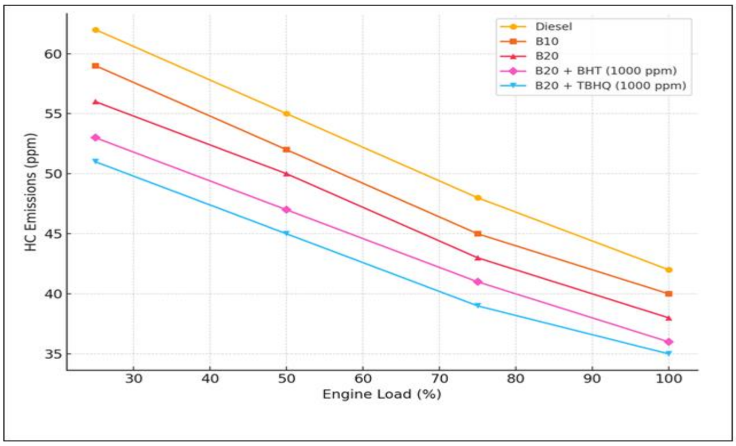

Fig. 6. Variation of HC Emissions with Engine Load

IV.vi. Smoke Opacity

Smoke opacity results are presented in Figure 7. Smoke emissions increased with load for all fuels because of the higher fuel injection rate and reduced air–fuel ratio at elevated loads. Biodiesel blends produced lower smoke emissions than diesel due to their inherent oxygen content, which aids soot oxidation during combustion. The addition of antioxidants further reduced smoke opacity. The B20 + TBHQ (1000 ppm) blend exhibited the lowest smoke opacity (22%) compared to 28% for diesel and 26% for untreated B20. The reduction is attributed to the improved combustion and suppression of soot precursors by antioxidants, which facilitate more complete oxidation of hydrocarbons and carbonaceous particulates [18].

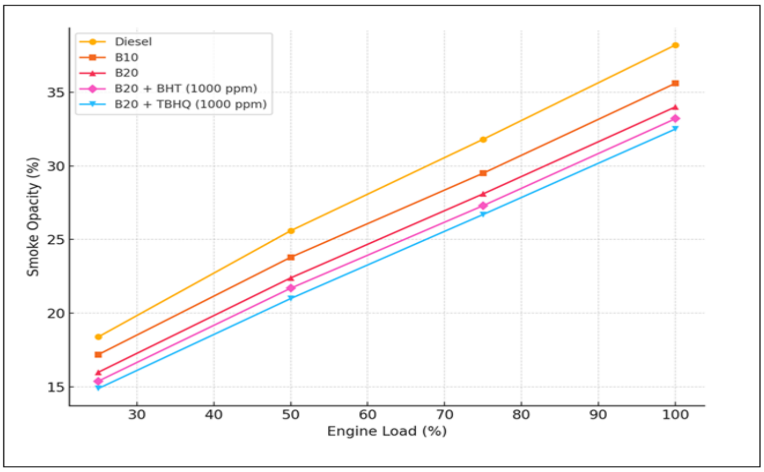

Fig. 7. Variation of Smoke Opacity with Engine Load

IV, vii. Cylinder Pressure Analysis

The variation of in-cylinder pressure with crank angle provides valuable insights into the combustion process of biodiesel–antioxidant blends in the CRDI engine. Figure 8 illustrates the cylinder pressure traces for diesel, untreated biodiesel (B20), and antioxidant-treated biodiesel blends (B20 + BHT and B20 + TBHQ) at full load and 1500 rpm engine speed. The cylinder pressure increased during the compression stroke and reached its peak near top dead center (TDC), indicating the occurrence of premixed combustion [24]. For all fuels, the combustion process exhibited a typical diesel engine profile consisting of ignition delay, premixed burning, and diffusion burning phases. The peak cylinder pressure (Pmax) for diesel was observed to be 71 bar, while for the B20 blend it was slightly lower at 68 bar, owing to biodiesel's higher viscosity and slower vaporization, which delays the mixing-controlled combustion phase. When antioxidants were added, a noticeable improvement in cylinder pressure was observed. The B20 + TBHQ (1000 ppm) blend exhibited a peak pressure of 70.5 bar, very close to diesel, while B20 + BHT (1000 ppm) recorded 69.2 bar. This enhancement in peak pressure for antioxidant-treated fuels indicates improved ignition quality and combustion efficiency. Antioxidants stabilize the fuel by preventing peroxide and radical formation, which helps maintain consistent combustion and better atomization characteristics. The observed increase in pressure also suggests a reduction in ignition delay and enhanced combustion kinetics due to the antioxidant's influence on fuel reactivity. At higher antioxidant concentrations (2000 ppm), a marginal decrease in peak pressure was noted. This may be attributed to excess additive presence, which can slightly alter fuel volatility and affect the premixed combustion phase. Therefore, the optimum concentration of 1000 ppm proved most effective in enhancing cylinder pressure characteristics. The combustion phasing (crank angle corresponding to Pmax) for all biodiesel blends occurred slightly earlier than diesel, which can be explained by the higher cetane number and oxygen content of biodiesel. Early combustion phasing generally contributes to higher in-cylinder temperatures and improved efficiency at moderate loads, but may also influence NOx emissions at full load. Overall, the B20 + TBHQ (1000 ppm) blend demonstrated the most favorable pressure development, with smooth and complete combustion comparable to diesel fuel. This confirms that the use of appropriate antioxidant concentrations not only improves fuel stability but also promotes better combustion behavior in CRDI diesel engines [19].

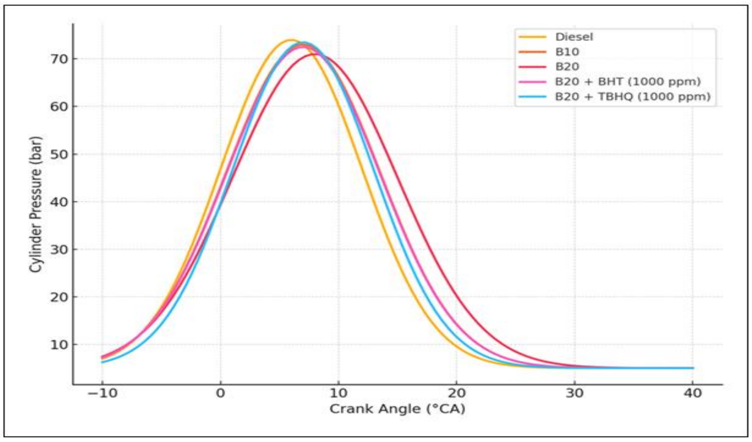

Fig. 8. Variation of In-Cylinder Pressure with Crank Angle

IV.viii. Heat Release Rate (HRR) Analysis

The Heat Release Rate (HRR) is a crucial combustion parameter that provides detailed insight into the rate of energy liberation during the combustion process. It helps in understanding ignition delay, combustion phasing, and the influence of fuel properties and additives on combustion efficiency. The HRR was calculated from the in-cylinder pressure data using the first law of thermodynamics, expressed as:

$$\frac{dQ_{net}}{d\theta} = \frac{\gamma}{\gamma-1} P \frac{dV}{d\theta} + \frac{1}{\gamma-1} V \frac{dP}{d\theta}$$

For diesel, the HRR peak occurred at approximately 6° after TDC (ATDC), with a maximum value of 72 J/°CA. For the untreated B20 blend, the peak shifted slightly earlier to 5° ATDC with a reduced magnitude of 65 J/°CA. The earlier occurrence of the peak is due to the higher cetane number and oxygenated nature of biodiesel, which promotes faster ignition and enhanced combustion of the premixed charge. Upon addition of antioxidants, particularly TBHQ (1000 ppm), the HRR peak increased to 70 J/°CA, closely matching diesel. This indicates improved combustion efficiency and enhanced energy release due to better fuel oxidation and reduced peroxide formation. The addition of BHT (1000 ppm) also showed improvement, but to a lesser extent (68 J/°CA). The improvement in HRR is attributed to the stabilizing effect of antioxidants on fuel molecules, leading to more uniform atomization and controlled combustion within the cylinder. The results suggest that antioxidant-treated biodiesel improves the premixed combustion phase, leading to faster and more complete combustion. This finding aligns with the observations of [20,21], who also reported that antioxidants enhance the combustion rate and stability of biodiesel fuels.

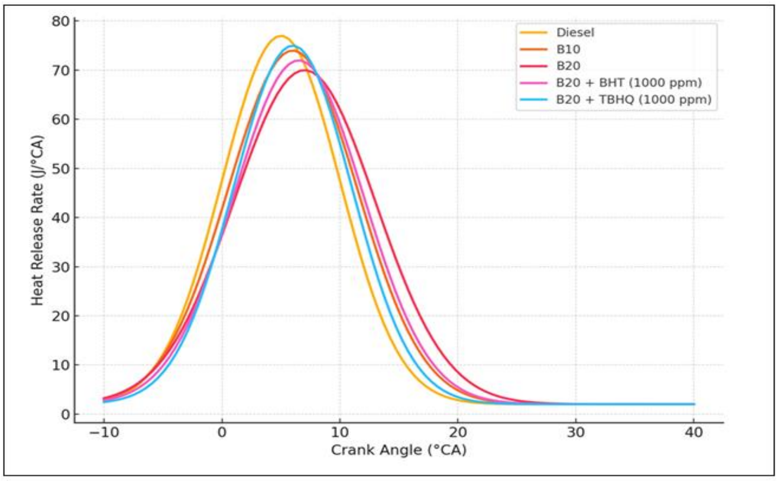

Fig. 9. Variation of Heat Release Rate with Crank Angle

V. Conclusion

The experimental investigation on the performance, combustion, and emission characteristics of a CRDI diesel engine fueled with biodiesel blends incorporated with antioxidant additives revealed significant improvements in overall engine behavior. The results showed that the addition of antioxidants such as

Butylated Hydroxytoluene (BHT) and Tertiary Butylhydroquinone (TBHQ) to the B20 biodiesel blend enhanced fuel oxidation stability and combustion efficiency. The B20 + TBHQ (1000 ppm) blend exhibited superior performance, achieving a higher brake thermal efficiency and lower brake specific fuel consumption compared to untreated biodiesel, approaching the efficiency of diesel fuel. Combustion analysis indicated that the antioxidant-treated blends produced smoother pressure traces and higher heat release rates, confirming improved ignition quality and more complete combustion. In terms of emissions, biodiesel blends emitted lower levels of CO, HC, and smoke opacity than diesel, while the inclusion of antioxidants further reduced these emissions and slightly mitigated NOx formation. Overall, the B20 + TBHQ blend demonstrated the most balanced performance across efficiency, combustion, and emission parameters, suggesting that the use of antioxidant additives can effectively enhance the suitability of biodiesel for modern CRDI diesel engines without requiring engine modification.

Conflict of Interest:

There was no relevant conflict of interest regarding this paper.

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