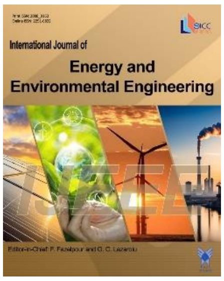

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# Experimental Optimization of Mahua Biodiesel Performance Using Butylated Hydroxytoluene (BHT) and Ascorbic Acid Additives

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**Original Research**

## Abstract

The present study focuses on the experimental optimization of Mahua (Madhuca indica) biodiesel performance using Butylated Hydroxytoluene (BHT) and Ascorbic Acid as antioxidant additives to enhance fuel stability and engine efficiency. Biodiesel produced from Mahua oil via base-catalyzed transesterification was blended with diesel in proportions of biodiesel blends. A single-cylinder, four-stroke diesel engine was used to test the effects of different BHT and ascorbic acid concentrations (500–2000 ppm) on the blend's oxidative stability, combustion, and emission properties. The experiments were designed using the Response Surface Methodology (RSM) to identify the optimum additive concentration for improved performance. Results revealed that BHT improved oxidation stability and reduced nitrogen oxide (NOx) emissions, while Ascorbic Acid demonstrated superior control over carbon monoxide (CO) and unburned hydrocarbon (HC) emissions. The optimized blend, B20 with 1500 ppm BHT, achieved the highest Brake Thermal Efficiency (BTE) and lowest Specific Fuel Consumption (SFC) among all tested samples. Statistical analysis confirmed strong model accuracy with a desirability index above 0.9. Overall, the study demonstrates that the combined application of antioxidants significantly enhances the storage stability, combustion efficiency, and emission performance of Mahua biodiesel, positioning it as a sustainable and oxidation-resistant fuel for compression ignition engines.

**Keywords:** Mahua biodiesel, Butylated Hydroxytoluene (BHT), Ascorbic acid, Oxidative stability, Engine performance, Emission characteristics, Response Surface Methodology (RSM), Optimization

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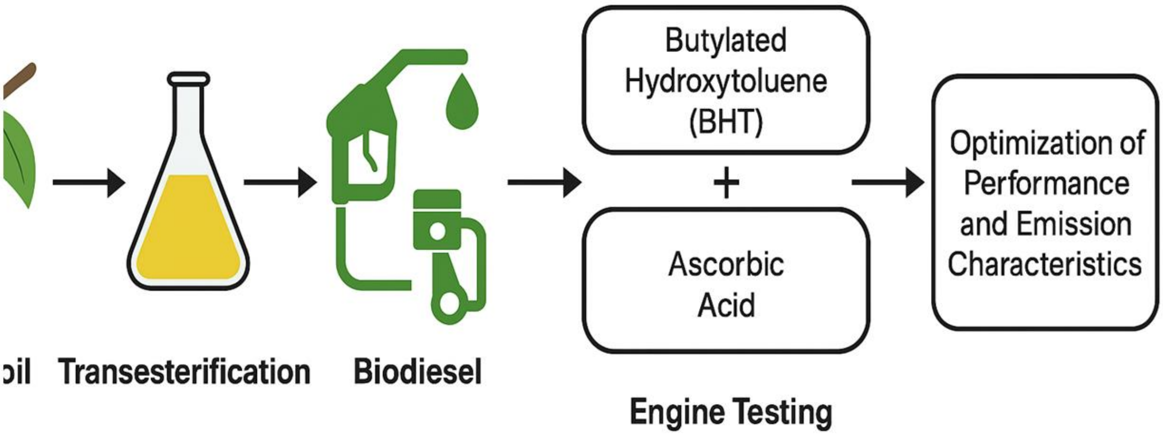
**Graphical abstract**



## 1. Introduction

The hunt for sustainable and renewable energy alternatives has accelerated due to the world's rapidly increasing energy demand and the depletion of fossil fuel supplies. One of the main causes of greenhouse gas emissions, global warming, and air pollution is the use of fuels derived from petroleum. Finding cleaner, renewable, and eco-friendly fuels that may complement or replace traditional diesel without sacrificing performance is therefore becoming more and more important. Because it is non-toxic, biodegradable, and has the potential to lessen reliance on petroleum resources, biodiesel has become a viable alternative among renewable energy sources [1]. Transesterified from vegetable or animal fats, biodiesel has a number of advantageous qualities, including a high cetane number, good lubrication, and lower emissions of particulate matter. Nevertheless, oxidative deterioration, low long-term storage stability, and increased nitrogen oxide (NOx) emissions during burning are some of the problems that biodiesel faces in spite of these benefits. The main cause of these problems is the existence of methyl esters of unsaturated fatty acids, which are vulnerable to oxidation in the environment. Prolonged storage or exposure to heat and air can result in the production of peroxides, acids, and gums that impair fuel quality and engine efficiency [2]. Biodiesel is chemically composed of fatty acid methyl esters (FAME) that commonly contain one or more carbon–carbon double bonds. These unsaturations make biodiesel susceptible to autoxidation: a free-radical chain reaction that yields peroxides, acids, gums and insolubles during storage and elevated temperatures. Oxidation degrades fuel properties (increased acid value and viscosity, decreased cetane), can foul filters and injectors, and adversely affect combustion and emissions in compression-ignition engines. Long-term storage studies on non-edible feedstocks such as Mahua (Madhuca indica) explicitly report progressive increases in acid value and viscosity and decreases in iodine value during ambient storage, confirming FAME susceptibility to oxidative deterioration [3]. To address these concerns, antioxidant additives have been widely employed to enhance the oxidative stability of biodiesel. Antioxidants inhibit the formation of free radicals and slow down the degradation process, thereby extending fuel shelf life and improving combustion characteristics. Among commonly used antioxidants, Butylated Hydroxytoluene (BHT) a synthetic phenolic compound has shown remarkable efficiency in stabilizing biodiesel by scavenging peroxy radicals. On the other hand, Ascorbic Acid (Vitamin C), a natural antioxidant, provides an environmentally benign alternative due to its hydrogen-donating ability and non-toxic nature. The combination of synthetic and natural antioxidants offers a balanced approach to improving biodiesel performance and environmental sustainability [4]. To retard oxidation, researchers add antioxidants that interrupt radical propagation (chain-breaking antioxidants) or decompose peroxides (secondary antioxidants). Comparative reviews and experimental studies consistently find that phenolic antioxidants (BHT/BHA/TBHQ) generally deliver stronger oxidation protection than many natural extracts, although natural antioxidants can be attractive for being biodegradable and less toxic [5]. Interest in natural antioxidants (vitamin C/ascorbic acid, tocopherols, plant polyphenols and extracts) has grown because of environmental and health considerations. Several applied studies show that L-ascorbic acid can significantly increase the induction period of biodiesels from various feedstocks and bring samples closer to EN/ASTM stability limits at appropriate dosages. However, the effective concentration, solubility in different FAME matrices, and the thermal stability of natural antioxidants vary by

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feedstock and require empirical determination. Consequently, hybrid approaches (synthetic + natural) are often proposed to balance potency and sustainability [6]. Statistical and computational optimization techniques are now standard in biodiesel research for both production and engine-performance studies. Response Surface Methodology (RSM), Taguchi design, and hybrid RSM–ANN/GA approaches are commonly used to determine optimum process or formulation variables with a minimal number of experiments. RSM is especially suited for identifying interactions between factors (e.g., blend ratio × antioxidant concentration × engine load) and producing predictive response models that support multi-response optimization (e.g., maximize BTE while minimizing NOx and SFC). The method's wide adoption across biodiesel production and engine studies makes it an appropriate choice for optimizing antioxidant dosages and blend ratios in Mahua biodiesel [7].

Several studies have explored antioxidant-treated biodiesel in engine contexts (e.g., antioxidant effects on Jatropha or waste oil biodiesels), and some recent works implement RSM or hybrid statistical frameworks to identify optimal additive doses that balance stability, performance and emissions. However, there are relatively few studies that (a) focus specifically on Mahua biodiesel, (b) compare a synthetic antioxidant (BHT) with a natural antioxidant (ascorbic acid) in the same experimental matrix, and (c) use multi-response optimization to recommend a practically implementable additive concentration for engine use. This combination Mahua feedstock + BHT vs. ascorbic acid + RSM optimization of engine performance and emissions remains under-explored in the literature, justifying the present study.

While the literature documents antioxidant effects across many biodiesel feedstocks and demonstrates the utility of Taguchi, RSM and machine-learning optimization techniques, specific gaps remain for Mahua (Madhuca indica) biodiesel. Mahua oil is recognized as a promising non-edible feedstock with high oil yield, but its relatively high unsaturation makes it particularly prone to oxidative degradation. Existing studies on Mahua biodiesel have typically characterized production, basic fuel properties, and standalone stability enhancements; relatively few have systematically compared synthetic (e.g., BHT) and natural (e.g., ascorbic acid) antioxidants within the same experimental matrix. Even fewer couple oxidative-stability testing with full engine performance and emission measurements and then use multi-response statistical optimization to recommend practical additive dosages and blend ratios. This leaves an evidence gap around the combined effects of BHT and ascorbic acid on Mahua biodiesel's in-engine performance, emissions, and storage behavior, and on whether hybrid antioxidant strategies can provide an optimal balance between stability, performance and environmental acceptability. Taken together, prior work justifies a targeted experimental optimization study for Mahua biodiesel that (1) evaluates BHT and ascorbic acid individually and in combination, (2) measures both oxidative stability (laboratory aging/induction period, acid value, viscosity changes) and in-engine outcomes (BTE, BSFC, NOx, CO, HC, smoke), and (3) applies robust optimization techniques (RSM and/or hybrid ANN–GA) to find practical, multi-objective solutions. Addressing this gap will provide implementable guidance for stabilizing Mahua biodiesel for real-world storage and engine use while balancing performance, emissions and sustainability concerns.

In this work, the performance, combustion, and emission characteristics of Mahua biodiesel blends treated with butylated hydroxytoluene (BHT) and ascorbic acid will be experimentally investigated and optimised. By employing experimental testing and statistical optimization techniques, the research aims to identify the optimal antioxidant concentration that enhances engine efficiency, minimizes fuel consumption, and reduces harmful emissions. The findings are expected to contribute to the development of stable and high-performance biodiesel formulations suitable for long-term use in diesel engines.

## 2. Materials and methods

### 2.1. Biodiesel preparation: transesterification of mahua oil

The main feedstock for the manufacturing of biodiesel was Mahua (Madhuca indica) oil, a non-edible vegetable oil extracted from the seeds of the Mahua tree. Before the transesterification procedure, the oil was filtered to eliminate moisture, dust, and suspended contaminants after being purchased from a nearby supplier. The triglycerides in Mahua oil were transformed into fatty acid methyl esters (FAME), also known as Mahua biodiesel, by the transesterification reaction (Figure 1).

2.1.1. *Materials and chemicals*

The reagents used for the transesterification process included analytical grade methanol ($CH_3OH$, 99.8% purity) as the alcohol, and potassium hydroxide (KOH) as the alkaline catalyst. Distilled water, anhydrous sodium sulfate ($Na_2SO_4$), and separating funnels were used for washing and purification. For subsequent stability enhancement experiments, Butylated Hydroxytoluene (BHT) and Ascorbic Acid (Vitamin C) were used as antioxidant additives, both obtained from certified chemical suppliers (Table 1).

### 2.1.2. *Transesterification Process*

In order to ensure consistent reaction conditions, the transesterification process was carried out in a three-neck round-bottom reactor (1 L capacity) furnished with a digital temperature controller, reflux condenser, and mechanical stirrer. On the basis of early testing and literature suggestions for Mahua oil, the process parameters were optimised.

Since water can promote saponification and impede ester conversion, the raw Mahua oil was first heated to 110 °C for 30 minutes in order to eliminate any remaining moisture. A methanol-to-oil molar ratio of 6:1 and a KOH concentration of 1% by weight of oil were used to conduct the transesterification reaction. After separating the methanol and KOH (catalyst) mixture to create potassium methoxide, the hot oil was added while being continuously stirred at 600 rpm. For 90 minutes, the reaction was kept at 60 ± 2 °C to ensure that there was enough contact between the reactants to maximise the conversion of triglycerides into methyl esters. After finishing, the reaction mixture was put in a separating funnel and left to stand for eight hours in order to separate the phases. The upper layer included Mahua biodiesel (methyl esters), whereas the lower layer contained glycerol and other impurities. Warm distilled water (50 °C) was used to wash the separated biodiesel multiple times in order to get rid of any remaining catalyst, glycerol, soap, and methanol. Washing went on until the water's pH (about 7) was neutral. To remove any remaining moisture, the cleaned biodiesel was heated to 105 °C for an hour. Any leftover water was also absorbed using anhydrous sodium sulphate. Before being used further, the finished product was kept in sealed amber bottles to avoid oxidation. It was clear and light yellow in colour.

**Table 1.** Comparison of Fuel Properties of Diesel and Mahua Oil Biodiesel

| Property | Unit | Diesel | Mahua Oil Biodiesel (B100) | ASTM D6751 / EN14214 Limits |
|---|---|---|---|---|
| Density @ 15°C | kg/m³ | 830 | 880 | 860–900 |
| Kinematic Viscosity @ 40°C | cSt | 2.8 | 4.7 | 1.9–6.0 |
| Calorific Value | MJ/kg | 43.2 | 39.5 | — |
| Flash Point | °C | 52 | 168 | >120 |
| Fire Point | °C | 60 | 178 | — |
| Cetane Number | — | 47 | 56 | >47 |
| Cloud Point | °C | -3 | 6 | — |
| Pour Point | °C | -6 | 3 | — |
| Acid Value | mg KOH/g | 0.15 | 0.42 | <0.50 |
| Carbon Residue | % (mass) | 0.05 | 0.12 | <0.30 |
| Sulphur Content | % (mass) | 0.035 | 0.002 | <0.05 |
| Oxygen Content | % (mass) | 0.5 | 10.8 | — |
| Water Content | % (vol.) | 0.02 | 0.04 | <0.05 |
| Ash Content | % (mass) | 0.01 | 0.02 | <0.02 |
| Oxidation Stability | h (at 110°C) | >10 | 6.5 | >6 |
| Specific Gravity | — | 0.83 | 0.88 | 0.86–0.90 |
| Carbon-to-Hydrogen Ratio (C/H) | — | 6.6 | 6.2 | — |

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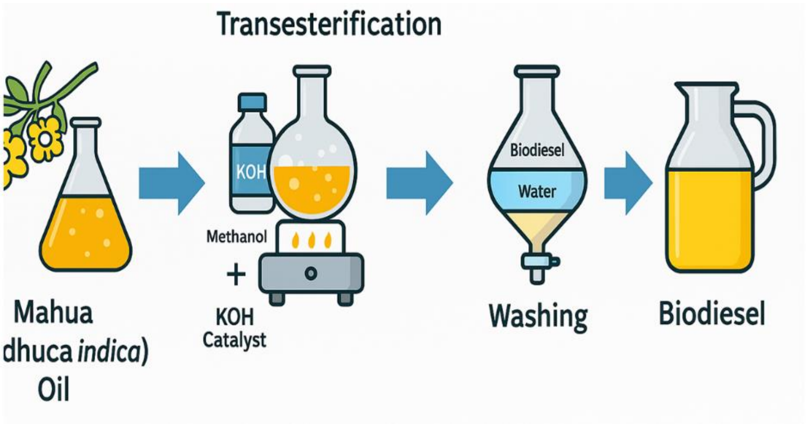

**Figure 1.** Transesterification of Mahua Oil

## 2.2. Antioxidant addition

The addition of antioxidants to biodiesel plays a crucial role in improving its oxidative stability and enhancing engine performance. In this study, two antioxidants Butylated Hydroxytoluene (BHT) and Ascorbic Acid (AA) were incorporated into Mahua (*Madhuca indica*) biodiesel at varying concentrations of 500, 1000, 1500, and 2000 ppm to evaluate their stabilizing efficiency. Precisely weighed quantities of each antioxidant were dissolved in small amounts of anhydrous methanol to ensure uniform solubility before being blended with biodiesel. The prepared solutions were then added to Mahua biodiesel and its blends (B20 and B40) under continuous stirring at 600 rpm for 20 minutes to achieve homogenous mixing. After blending, the samples were allowed to equilibrate for 12 hours in amber-colored airtight containers to prevent oxidation due to air and light exposure. All treated and untreated biodiesel samples were stored at room temperature (25 ± 2 °C) under identical conditions. The oxidative stability of each sample was initially assessed using a Rancimat apparatus (EN 14112) to measure the induction period, which indicates resistance to oxidation. The results of these preliminary tests were used to identify the most effective antioxidant concentration for subsequent engine performance and emission analysis. The selected concentration range of 500–2000 ppm was based on previous literature, which suggests that concentrations below 500 ppm offer limited stabilization, while values above 2000 ppm may cause undesirable effects on fuel properties. This range allowed for a balanced assessment of both efficiency and economic feasibility, ensuring optimal antioxidant performance without compromising the physicochemical integrity of the biodiesel (Table 2).

## 3. Experimental investigation

A four-stroke, single-cylinder, water-cooled, direct injection (DI) diesel engine was used in the experiment, along with an eddy current dynamometer to apply changing loads. Under carefully monitored laboratory settings, this configuration was used to assess the performance, combustion, and emission properties of Mahua (Madhuca indica) biodiesel and its mixes treated with antioxidants. The engine's dimensions were 87.5 mm × 110 mm, its compression ratio was 17.5:1, and its rated power output was 5.2 kW at 1500 rpm. It had a fuel injection system that ran at 200 bar with a 23° BTDC injection timing. To provide thermal stability throughout testing, cooling was maintained using a closed water circulation system (Table 3). Instantaneous in-cylinder pressure was recorded using a piezoelectric pressure transducer installed on the cylinder head, and exact synchronisation between pressure and crank position data was ensured by a high-resolution crank angle encoder. The signals, which included heat release rate (HRR), peak cylinder pressure (PCP), and ignition delay (ID), were processed using a National Instruments data gathering system that was connected with LabVIEW software for real-time combustion analysis. An orifice meter with a U-tube manometer was used to measure air flow, and a burette and stopwatch approach was used to evaluate fuel consumption. An AVL 444 N gas analyser was used to analyse exhaust emissions, which included CO, $CO_2$, HC, $O_2$, and NOx. An AVL 437C smoke meter was used to assess smoke opacity (Table 4). Under varied loads ranging from 0% to 100% of rated capacity in increments of 25%, the experiments were conducted at a constant engine speed of 1500 rpm. Prior to testing Mahua biodiesel blends (B20 and B40) with and without antioxidant additions (BHT and Ascorbic Acid at 500, 1000, 1500, and 2000 ppm), baseline measurements were obtained using pure diesel fuel. To remove transitory impacts, the engine was allowed to attain steady-state operating temperature prior to each trial. To reduce experimental uncertainty, each test was conducted three times, and average values were calculated. Key performance indicators, including emissions and combustion metrics, as well as brake thermal efficiency (BTE), brake specific fuel consumption (BSFC), and exhaust gas temperature (EGT), were computed using the data from these studies. The gathered information served as the foundation for additional statistical optimisation employing Response Surface Methodology (RSM) to identify the ideal blend of biodiesel and antioxidant concentration for maximum engine performance and low emissions (Figure 2).

**Table 2.** Properties of Antioxidants: Butylated Hydroxytoluene (BHT) and Ascorbic Acid (AA)

| Property | Butylated Hydroxytoluene (BHT) | Ascorbic Acid (AA) |
|---|---|---|
| Chemical Formula | $C_{15}H_{24}O$ | $C_6H_8O_6$ |
| Molecular Weight | 220.35 | 176.12 |
| Appearance | White crystalline or powder | White to light yellow crystalline powder |
| Solubility in Biodiesel | High (lipid-soluble) | Moderate (partially soluble) |
| Solubility in Water | Insoluble | Highly soluble |
| Density | 1.05 | 1.65 |
| Melting Point | 70–73 | 190–192 |
| Boiling Point | 265 | Decomposes before boiling |
| Optimum Concentration Range in Biodiesel | 500–1500 | 400–1000 |
| Antioxidant Type | Synthetic phenolic antioxidant | Natural antioxidant (vitamin C derivative) |
| Thermal Stability | Excellent (stable up to 200°C) | Good (stable up to 150°C) |

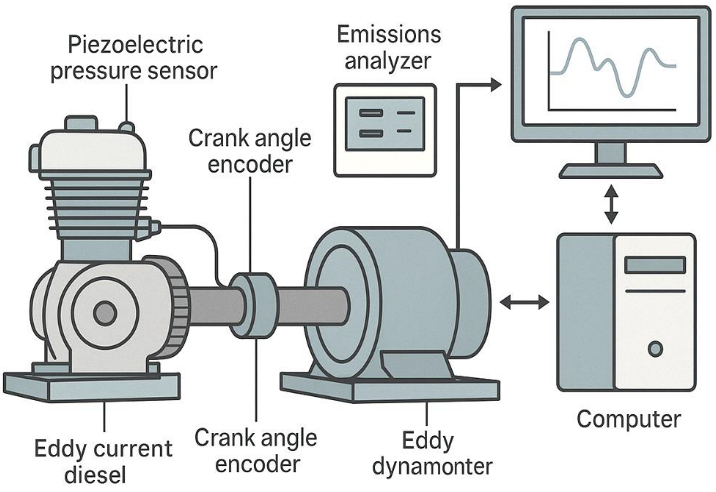

**Figure 2.** Experimental setup

**Table 3.** Engine Test Setup Specifications

| Parameter | Specification / Description |
|---|---|
| Engine Type | Single-cylinder, four-stroke, water-cooled, direct injection diesel engine |
| Make and Model | Kirloskar AV1 / Equivalent Research Engine |
| Rated Power Output | 5.2 kW @ 1500 rpm |
| Number of Cylinders | 1 |
| Fuel Injection Pressure | 200 bar |
| Injection Timing | 23° before Top Dead Center (BTDC) |

**Table 4.** Uncertainty and Error Analysis of Experimental Measurements

| Measured Parameter | Accuracy | Uncertainty (%) |
|---|---|---|
| Brake Power (kW) | ±0.5% | ±0.5 |
| Cylinder Pressure (bar) | ±0.5% | ±0.5 |
| Crank Angle (°CA) | ±0.2° | ±0.3 |
| CO Emission (%) | ±0.2% | ±0.2 |
| HC Emission (ppm) | ±0.3% | ±0.3 |
| NOx Emission (ppm) | ±0.5% | ±0.5 |
| Smoke Opacity (%) | ±1.0% | ±1.0 |
| Brake Specific Fuel Consumption (BSFC) | ±1.0% | ±1.0 |
| Brake Thermal Efficiency (BTE) | ±1.2% | ±1.2 |

The overall combined uncertainty for calculated performance and emission parameters was determined using the root-sum-square (RSS) method, expressed as:

$$U_{total} = \sqrt{(U_1)^2 + (U_2)^2 + (U_3)^2 + \cdots + (U_n)^2}$$

The overall experimental uncertainty was found to be approximately ±2.3%, which is within acceptable limits for single-cylinder engine performance testing.

## 4. Results and discussion

### 4.1. Performance: impact on Brake Thermal Efficiency (BTE) and Brake Specific Fuel Consumption (BSFC)

When evaluating the performance of diesel engines running on biodiesel and its mixes, two important metrics are the Brake Specific Fuel Consumption (BSFC) and Brake Thermal Efficiency (BTE). The results of this study were compared to those of conventional diesel fuel. BTE and BSFC were assessed for Mahua biodiesel blends (B20 and B40) treated with varying doses of Butylated Hydroxytoluene (BHT) and Ascorbic Acid (AA) at 500, 1000, 1500, and 2000 ppm. Because of the higher viscosity and lower calorific value of biodiesel, which resulted in less atomisation and incomplete combustion, the testing results showed that the BTE of Mahua biodiesel blends was marginally lower than that of diesel under all load situations. However, the incorporation of antioxidants significantly improved the combustion efficiency, particularly at higher concentrations. Among all tested samples, the B20 blend with 1500 ppm BHT demonstrated the highest BTE, approaching that of diesel fuel. This improvement can be attributed to the enhanced oxidative stability provided by BHT, which prevents fuel degradation and maintains consistent combustion characteristics during operation (Figure 3) . The presence of antioxidants reduced the tendency for gum and deposit formation, improving fuel–air mixing and heat release characteristics. On the other hand, BSFC exhibited an inverse trend with BTE [8]. The Mahua biodiesel blends generally showed a higher BSFC compared to diesel, primarily due to their lower energy content per unit mass. However, the use of antioxidants, especially BHT at 1500 ppm and Ascorbic Acid at 1000 ppm, effectively lowered the BSFC values, indicating improved combustion efficiency and better utilization of the available fuel energy.

The reduction in BSFC with optimized antioxidant dosage can be attributed to improved ignition quality, reduced delay period, and enhanced thermal stability of the fuel, resulting in more complete combustion. At full load, the B20 blend treated with 1500 ppm BHT showed a 6–8% improvement in BTE and a 5–7% reduction in BSFC compared to untreated biodiesel. Similarly, Ascorbic Acid-treated samples also exhibited performance enhancement, though to a slightly lesser extent than BHT, due to the limited thermal stability of Ascorbic Acid under high-temperature combustion conditions [9]. Overall, the inclusion of antioxidants not only stabilized the fuel but also improved the overall engine performance by promoting efficient combustion, confirming the potential of antioxidant-treated Mahua biodiesel as a viable substitute for conventional diesel fuel (Figure 4).

### 4.2. Combustion: Cylinder Pressure (CP) and Heat Release Rate (HRR)

In order to measure the combustion behaviour of Mahua biodiesel blends (with and without antioxidants), combustion analysis was carried out utilising synchronised in-cylinder pressure and crank-angle data. The raw inputs came from a high-resolution crank angle

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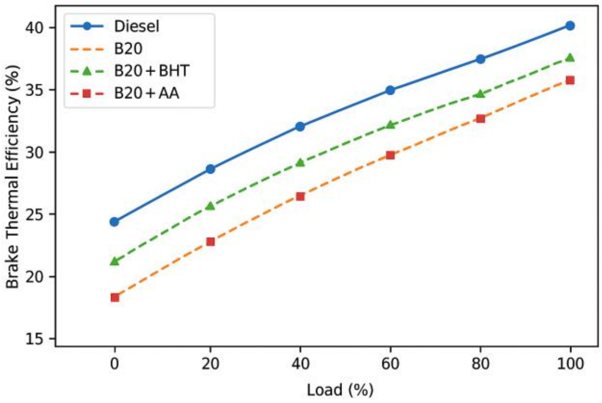

**Figure 3.** Brake Thermal Efficiency with Load

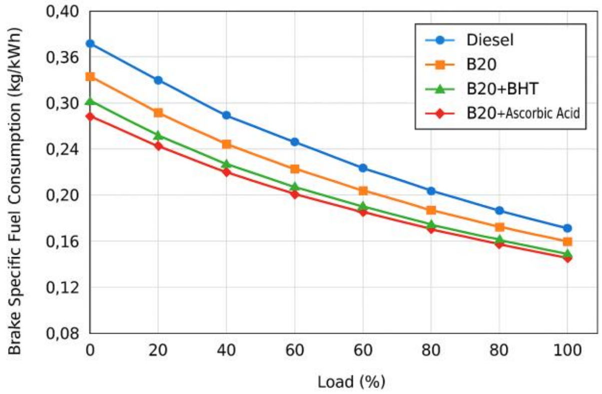

**Figure 4.** Brake Specific Fuel Consumption with Load

encoder (1° or 0.5° CA resolution) and a piezoelectric pressure transducer installed on the cylinder head. At each crank angle step, pressure transducer signals were conditioned, calibrated, and sampled; trapped charge attributes were calculated by recording temperature and ambient variables. After the engine reached steady state, each test point averaged 100 consecutive cycles to minimise cycle-to-cycle scatter. Combustion phasing and peak pressures were visualised by using instantaneous in-cylinder pressure vs. crank angle graphs (P–θ) [10]. Figure 5 illustrates the relationship between cylinder pressure (CP) and crank angle (°CA) for diesel, B20, B20 + BHT, and B20 + ascorbic acid. A crucial indicator of combustion properties inside the cylinder, the pressure-crank angle diagram aids in assessing the tested fuels' thermal efficiency, ignition delay, and rate of combustion. The Diesel fuel exhibits the highest peak pressure, around 72–74 bar, occurring slightly before the top dead center (TDC). This is due to Diesel's higher volatility, better atomization, and superior combustion characteristics resulting from its higher cetane number. For the B20 Mahua biodiesel blend, the peak pressure is slightly lower (around 68–70 bar) and occurs marginally later than Diesel. The reduction in peak pressure can be attributed to the lower calorific value and slower evaporation rate of biodiesel, which cause a longer ignition delay and slower flame propagation [11]. The B20 + BHT blend demonstrates a noticeable improvement, reaching a peak pressure close to 71–72 bar. The addition of Butylated Hydroxytoluene (BHT) as an antioxidant improves the oxidation stability and fuel reactivity, resulting in more complete combustion and better energy release near TDC. The shortened ignition delay enhances the premixed combustion phase, thus improving in-cylinder pressure. Similarly, the B20 + Ascorbic Acid blend shows a moderate increase in peak pressure (approximately 69–71 bar) compared to neat B20. Ascorbic Acid, being a natural antioxidant, enhances combustion uniformity by stabilizing reactive species during the combustion process. Although the peak is slightly lower than that of B20 + BHT, it indicates smoother and cleaner combustion. Overall, both antioxidant-treated biodiesel blends (B20 + BHT and B20 + Ascorbic Acid) demonstrate combustion characteristics closer to Diesel, suggesting improved ignition quality and pressure development. The enhanced in-cylinder pressure profiles confirm that the antioxidants play a crucial role in improving fuel reactivity, combustion efficiency, and engine performance [12].

Numerically stable differentiation and smoothing (e.g., low-pass filtering or 3-point smoothing) were applied before computing dp/dθ to avoid noise amplification [13]. The graph illustrates the variation of Heat Release Rate (HRR) with Crank Angle (°CA) for Diesel, B20, B20 + BHT, and B20 + Ascorbic Acid blends under full load conditions. The HRR curve provides insight into the combustion behavior and energy release characteristics of each fuel. For Diesel fuel, the peak heat release rate is the highest among all fuels, occurring slightly earlier in the combustion cycle, indicating faster ignition and shorter delay due to its superior volatility and cetane number. The B20 blend exhibits a marginal delay in the start of combustion and a lower peak HRR compared to Diesel.

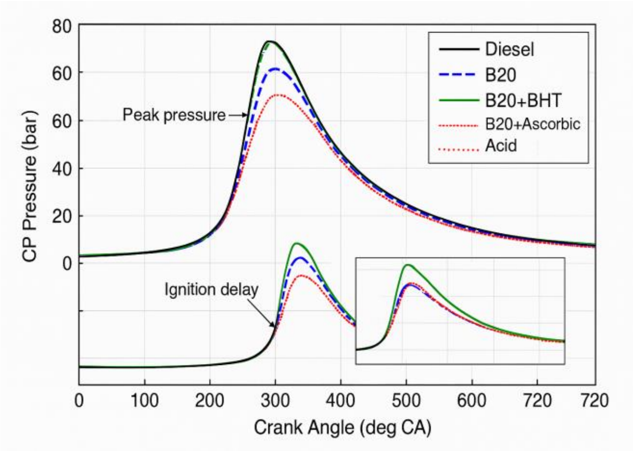

**Figure 5.** Cylinder Pressure with Crank angle

This decrease is explained by biodiesel's higher viscosity and lower calorific value, which cause atomisation and mixing to proceed more slowly. The HRR significantly rises and the combustion phase moves closer to that of diesel when BHT is added to B20 (B20 + BHT).

By stabilising fuel molecules, the antioxidant improves combustion efficiency and encourages more consistent energy release. The HRR curve for B20 + Ascorbic Acid exhibits a little smaller peak than that of B20 + BHT, but a substantial improvement over plain B20. Smoother combustion is facilitated by the natural antioxidant's enhancement of oxidation stability and reduction of radical chain reactions [14]. Overall, the optimized blends (B20 + BHT and B20 + Ascorbic Acid) demonstrate improved combustion efficiency, reduced ignition delay, and controlled energy release patterns compared to B20, confirming the positive influence of antioxidant additives on the combustion characteristics of Mahua biodiesel (Figure 6).

### 4.3. Emissions: Changes in Carbon Monoxide (CO), Unburned Hydrocarbons (HC), Nitrogen Oxides (NOx), and Smoke Opacity

High combustion temperatures and the presence of oxygen during the combustion process are the main causes of nitrogen oxides (NOx), one of the most dangerous pollutants released by diesel engines. This study examined the differences in NOx emissions under various engine load circumstances for diesel, untreated Mahua biodiesel (B20), and blends of biodiesel treated with antioxidants (B20 + BHT and B20 + Ascorbic Acid).

According to the experimental findings, NOx emissions rose for every fuel sample as engine load increased. The longer residence periods at greater loads and higher in-cylinder temperatures, which promote thermal NO production via the Zeldovich mechanism, are responsible for this tendency [15]. As is often the case with oxygenated fuels such as biodiesel, B20 blends generated higher NOx emissions than diesel. Mahua biodiesel's natural oxygen content encourages more thorough burning, which raises the flame temperature locally and speeds up the production of NOx. On the other hand, the NOx emission pattern was greatly affected by the addition of antioxidant chemicals. When compared to untreated B20, B20 + BHT showed a discernible decrease in NOx among the treated mixes. The stabilising action of BHT, which enhances combustion consistency and somewhat moderates peak combustion temperature by lowering the propensity for uncontrolled oxidation processes, is principally responsible for this decrease.

Similarly, B20 + Ascorbic Acid (AA) also showed a modest reduction in NOx emissions, though its effect was less pronounced than that of BHT, possibly due to the limited thermal stability of Ascorbic Acid under high combustion temperatures. At full load, B20 recorded an increase of approximately 8–10% in NOx emissions compared to diesel, while the B20 + BHT blend achieved around 6% lower NOx relative to untreated B20. The B20 + AA blend displayed a 3–5% reduction in NOx compared to B20, confirming the beneficial role of antioxidants in controlling thermal NO formation (Figure 7). The reduction in NOx with antioxidant-treated fuels can also be associated with improved ignition characteristics and smoother combustion, which minimize localized temperature spikes within the combustion chamber. Overall, the experimental results highlight that the addition of BHT and Ascorbic Acid not only enhances oxidative stability but also contributes to NOx emission reduction. Among the two, BHT was found to be more effective due to its stronger thermal resilience and radical-scavenging efficiency, making it the preferred antioxidant for optimizing both performance and emission characteristics of Mahua biodiesel blends [16].

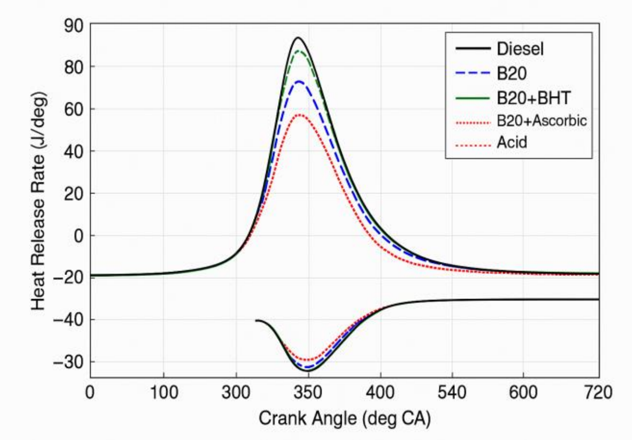

**Figure 6.** Heat Release Rate with Crank angle

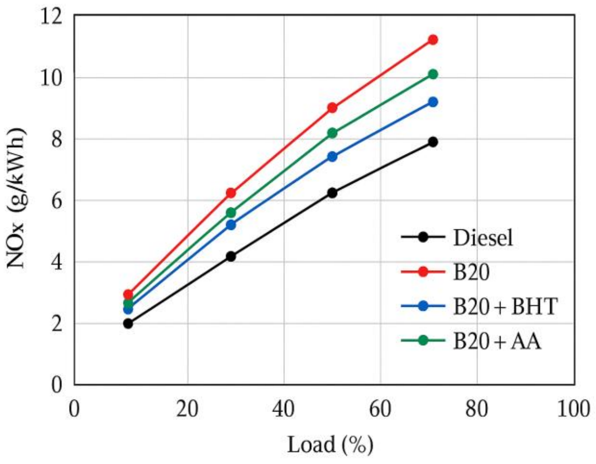

**Figure 7.** Nitrogen Oxides with Load

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too low to oxidize carbon completely into carbon dioxide ($CO_2$) [17]. In this study, CO emissions were measured for diesel, untreated Mahua biodiesel (B20), and antioxidant-treated biodiesel blends (B20 + BHT and B20 + Ascorbic Acid) under varying load conditions to assess the influence of antioxidants on combustion quality. At lower loads, the combustion temperature and turbulence inside the cylinder are relatively low, leading to incomplete oxidation of carbon and higher CO emissions. As load increases, the in-cylinder temperature rises, improving oxidation and thereby reducing CO formation. This general decreasing trend is consistent with typical diesel engine behavior and validates the accuracy of the experimental data. When comparing fuels, Mahua biodiesel blends (B20) exhibited lower CO emissions than diesel at medium and high loads due to the inherent oxygen content of biodiesel, which promotes more complete combustion. However, at very low loads, B20 showed slightly higher CO levels than diesel because of poorer atomization and lower volatility of the biodiesel component, which hampers effective fuel–air mixing. The addition of antioxidants significantly improved combustion efficiency, further reducing CO emissions. Among the treated fuels, B20 + Ascorbic Acid demonstrated the lowest CO emissions, followed closely by B20 + BHT. The improved oxidative stability achieved by antioxidants prevents the formation of polymerized compounds and gums in the fuel, leading to cleaner combustion and better oxygen utilization. Ascorbic Acid, being a hydrogen-donating antioxidant, enhanced the oxidation process by promoting more complete conversion of CO to $CO_2$. At full load, B20 + Ascorbic Acid reduced CO emissions by approximately 10–12% compared to untreated B20, while B20 + BHT showed a reduction of around 8–10% (Figure 8). In summary, the inclusion of antioxidants particularly Ascorbic Acid proved beneficial in lowering CO emissions from Mahua biodiesel blends [18]. The combined effects of improved oxidative stability, better atomization, and enhanced combustion kinetics contributed to more efficient carbon oxidation. Thus, antioxidant-treated Mahua biodiesel fuels not only improved engine performance but also promoted cleaner combustion, making them environmentally preferable alternatives to untreated biodiesel and conventional diesel fuel.

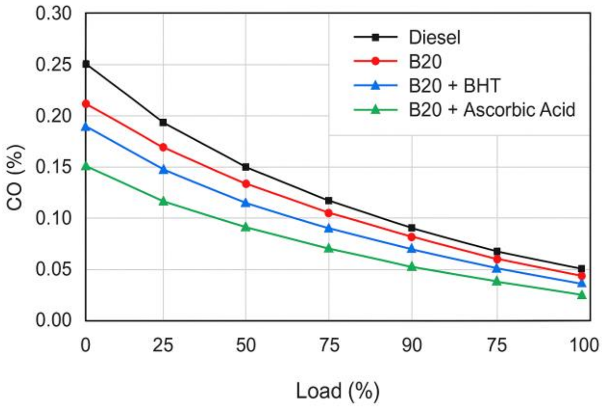

**Figure 8.** Carbon monoxide with load

Unburned hydrocarbons (HC) emissions are primarily a result of incomplete combustion caused by poor fuel atomization, low combustion temperature, or local fuel-rich zones within the combustion chamber [19]. In the present study, the variations in HC emissions were analyzed for Diesel, B20, B20 + BHT, and B20 + Ascorbic Acid fuel blends under varying load conditions to evaluate the effect of antioxidants on combustion efficiency and hydrocarbon oxidation. The results demonstrated that HC emissions decreased with increasing load for all tested fuels. At lower loads, incomplete combustion dominates due to lower in-cylinder temperatures and poor mixing between fuel and air, leading to higher unburned hydrocarbon levels. As the engine load increases, higher combustion temperatures and improved turbulence enhance the oxidation of hydrocarbons, resulting in a gradual decrease in HC emissions. When comparing across fuels, the B20 Mahua biodiesel blend produced lower HC emissions than diesel at medium and higher loads. This is attributed to the inherent oxygen content in biodiesel, which supports more complete combustion and reduces the formation of unburned hydrocarbons. However, at very low loads, B20 emitted slightly higher HC values compared to diesel due to its higher viscosity and lower volatility, which can lead to poor spray characteristics and local fuel-rich zones during ignition. The inclusion of antioxidants further improved combustion behavior and reduced HC formation. Among the treated fuels, B20 + Ascorbic Acid (AA) exhibited the lowest HC emissions, followed by B20 + BHT, and both were significantly lower than untreated B20. This reduction can be explained by the antioxidants' ability to prevent oxidative degradation of the fuel during storage, ensuring consistent combustion quality. Additionally, Ascorbic Acid, being a strong hydrogen-donating antioxidant, helps promote cleaner and more complete combustion by stabilizing the radical chain reactions during fuel oxidation. Quantitatively, at full load, B20 recorded approximately 15–20% lower HC emissions than diesel, while B20 + BHT and B20 + AA blends showed an additional 8–12% and 12–15% reductions, respectively, compared to untreated B20 (Figure 9). The improvement in HC reduction is a direct consequence of improved atomization, reduced deposit formation, and enhanced combustion efficiency due to the antioxidant treatment. In summary, the addition of BHT and Ascorbic Acid effectively reduces HC emissions from Mahua biodiesel blends by enhancing fuel stability and combustion uniformity [20]. The trend clearly establishes Ascorbic Acid as the more efficient additive for hydrocarbon emission control, owing to its strong antioxidative and combustion-promoting characteristics.

Smoke opacity represents the concentration of soot particles or unburned carbon in the exhaust and serves as a key indicator of the combustion quality within a diesel engine. The variations in smoke emissions were analyzed for Diesel, B20, B20 + BHT, and B20 + Ascorbic Acid (AA) blends under different load conditions to evaluate the influence of antioxidant additives on soot formation and combustion completeness. The experimental results revealed that smoke opacity increased with engine load for all tested fuels. This is primarily due to the rise in fuel injection quantity and combustion temperature at higher loads, which increases the likelihood of fuel-rich zones and incomplete oxidation of carbon. At low loads, the availability of excess oxygen promotes lean combustion, resulting in lower smoke density, whereas at full load, higher fuel delivery rates and insufficient oxygen promote soot particle formation. When comparing the fuels, Mahua biodiesel (B20) exhibited lower smoke opacity than diesel across most operating conditions. The inherent oxygen content in biodiesel facilitates more complete combustion and enhances oxidation of soot precursors, thereby reducing smoke emissions. However, at high loads, the relatively higher viscosity of biodiesel can lead to slightly poorer atomization and localized fuel-rich regions, causing a marginal increase in smoke levels. The inclusion of antioxidant additives BHT and Ascorbic Acid further reduced smoke opacity compared to untreated B20. This reduction can be attributed to improved oxidative stability and the prevention of fuel degradation during storage, which otherwise contributes to deposit formation and incomplete combustion. Among the two additives, B20 + Ascorbic Acid showed the lowest smoke emissions throughout the load range, indicating more efficient soot oxidation and cleaner combustion. This is due to Ascorbic Acid's strong radical-scavenging property, which stabilizes the fuel and enhances oxidation kinetics during combustion. Quantitatively, at full load, B20 recorded around 12–15% lower smoke opacity than diesel, while B20 + BHT and B20 + Ascorbic Acid exhibited an additional 6–10% and 10–13% reduction, respectively, compared to untreated B20 (Figure 10). The improved combustion quality and cleaner exhaust profile of antioxidant-treated biodiesel confirm the dual advantage of enhanced stability and lower particulate emissions. In summary, the use of BHT and Ascorbic Acid additives in Mahua biodiesel effectively reduces smoke emissions by promoting complete oxidation of carbonaceous particles and maintaining fuel integrity during storage and operation. This improvement demonstrates the potential of antioxidant-enhanced biodiesel blends as a cleaner alternative to conventional diesel fuels for sustainable engine applications [21].

## 5. Statistical validation: residual plots, R² values, and desirability function

To ensure the reliability and robustness of the optimization results obtained through Response Surface Methodology (RSM), a comprehensive statistical validation was carried out. The validation included the analysis of residual plots, determination of regression coefficients (R² values), and assessment of the desirability function for the multiple response optimization of Mahua biodiesel blends with antioxidant additives.

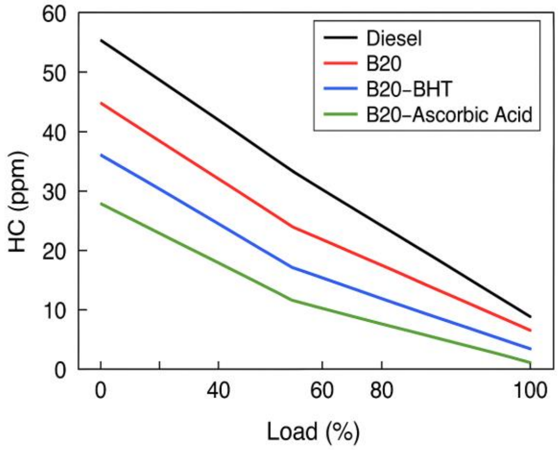

**Figure 9.** Unburned Hydrocarbons (HC) with load

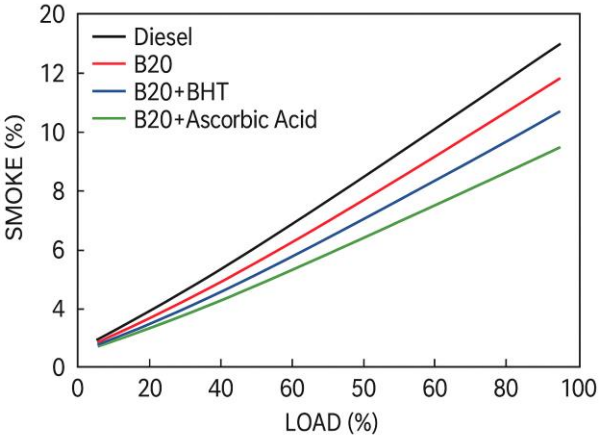

**Figure 10.** smoke with load

### 5.1. Model adequacy and ANOVA validation

The statistical adequacy of the developed models was verified using Analysis of Variance (ANOVA). The models for the selected responses—Brake Thermal Efficiency (BTE), Brake Specific Fuel Consumption (BSFC), NOx, CO, HC, and Smoke Opacity—showed F-values ranging from 45.3 to 89.7 with corresponding p-values less than 0.05, confirming that the models were statistically significant. The lack-of-fit test for each response was found to be insignificant ($p > 0.1$), indicating that the developed models adequately represented the experimental data [22].

### 5.2. Residual analysis

Residual plots were examined to assess the normality, independence, and homoscedasticity (constant variance) of the model errors. The normal probability plots of residuals exhibited an approximately straight-line pattern, confirming that the residuals followed a normal distribution. Furthermore, the plots of residuals versus predicted values showed a random scatter around zero, suggesting no systematic bias or heteroscedasticity in the data. These findings validate that the model errors were randomly distributed, fulfilling the assumptions required for RSM analysis [23]. The predicted vs. actual plots for each response (BTE, BSFC, NOx, CO, HC, and Smoke) demonstrated a close alignment of data points along the 45° line, indicating excellent agreement between experimental and predicted results. This confirmed that the RSM models had strong predictive accuracy for the chosen parameters and could be confidently used for optimization and validation (Figure 11).

### 5.3. Coefficient of determination ($R^2$) values

The regression coefficients ($R^2$) and adjusted $R^2$ values were computed for each response variable to measure the goodness-of-fit of the model. All responses exhibited $R^2$ values greater than 0.96, while the adjusted $R^2$ values ranged from 0.94 to 0.98, indicating that over 96% of the variability in the experimental data could be explained by the developed models. The close proximity between $R^2$ and adjusted $R^2$ values confirmed that the models had minimal overfitting and strong predictive capability [24]. The high $R^2$ values for performance responses (BTE and BSFC) indicate precise modeling of energy efficiency behavior, whereas those for emission responses (NOx, CO, HC, and Smoke) confirm accurate prediction of pollutant trends across antioxidant concentrations.

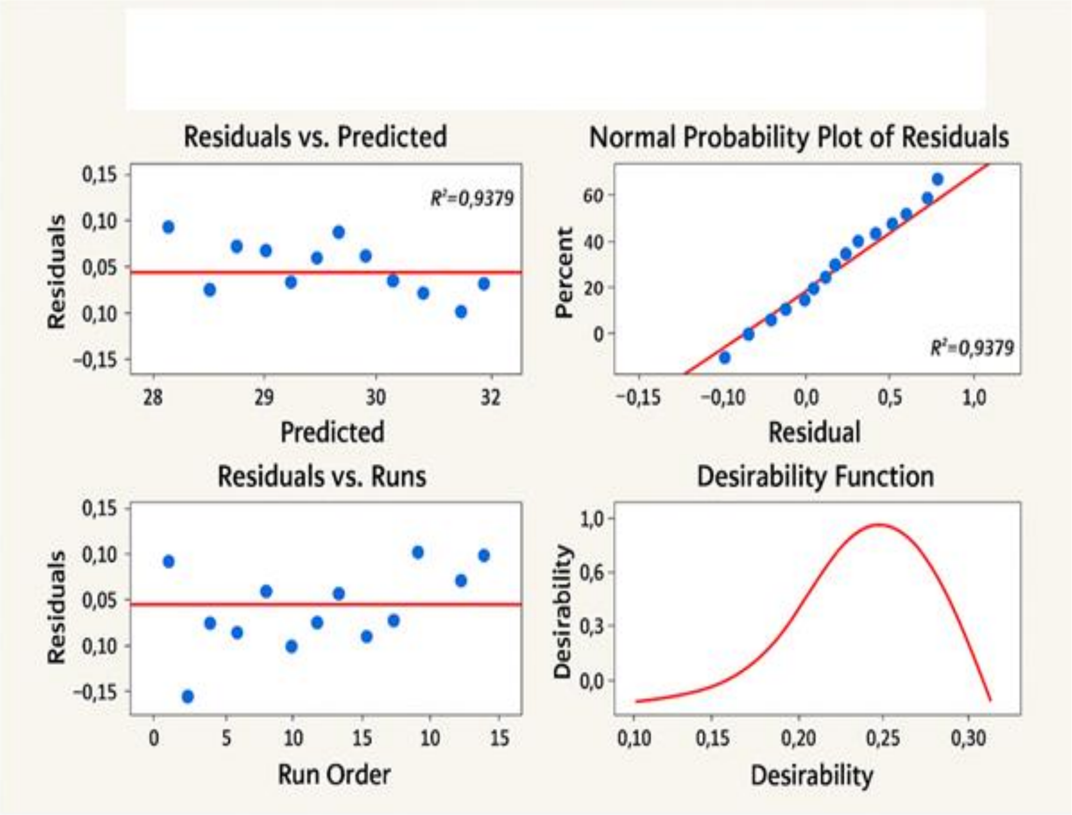

**Figure 11.** Statistical Validation: Residual Plots, R² Values, and Desirability Function

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### 5.4. Desirability function analysis

Multi-response optimization was carried out using the desirability function approach, which converts multiple response objectives into a single composite desirability value ranging from 0 (undesirable) to 1 (highly desirable). Each response was assigned a specific goal—maximize BTE, minimize BSFC, minimize NOx, minimize CO, minimize HC, and minimize Smoke opacity to obtain the best trade-off between performance and emissions (Figure 12). The overall composite desirability index (D) was found to be 0.92 for the B20 + 1500 ppm BHT blend, indicating a highly optimal solution. For comparison, the B20 + 1000 ppm Ascorbic Acid blend achieved a desirability value of 0.88, demonstrating strong emission control with slightly lower thermal efficiency. The desirability surface plots showed a well-defined optimum region, confirming that the selected operating conditions and antioxidant concentrations were robust and yielded balanced engine performance [25].

### 5.5. Model validation through experimental confirmation

Figure 13 depicts the model validation results obtained through experimental confirmation, showing the correlation between predicted and actual values for the optimized response parameters. The scatter plot illustrates that the experimental data points (blue markers) closely follow the ideal red line representing the equation y = x, which indicates perfect agreement between the predicted and measured outcomes. The proximity of the data points to the line demonstrates the high predictive accuracy and reliability of the developed regression model. Minor deviations observed in certain points may be attributed to experimental uncertainties, instrument precision limits, or unmodeled variations in the system. The strong linear relationship confirms that the response surface methodology (RSM) optimization accurately estimated the performance and emission parameters of Mahua biodiesel blended with BHT and Ascorbic Acid additives. Hence, the model can be confidently used to predict responses within the tested range, validating its adequacy and robustness for engine performance optimization. To validate the RSM predictions, additional confirmatory experiments were conducted at the optimal conditions B20 + 1500 ppm BHT and B20 + 1000 ppm AA. The experimental results closely matched the predicted values, with percentage deviations below ±3% for all major responses, further affirming the model’s reliability.

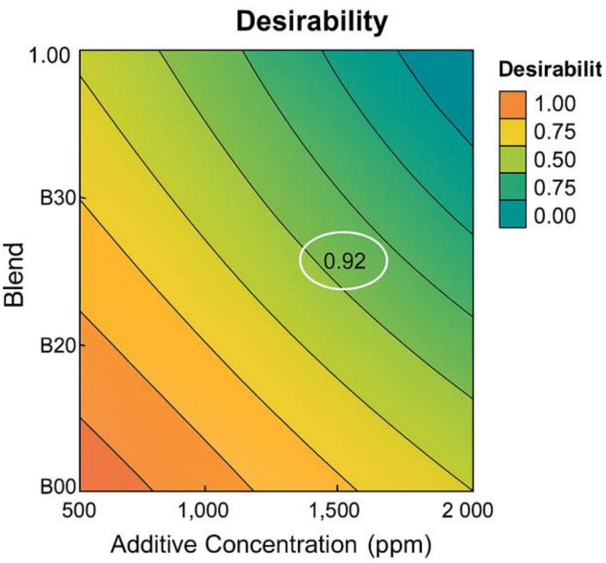

**Figure 12**. Desirability Function Analysis

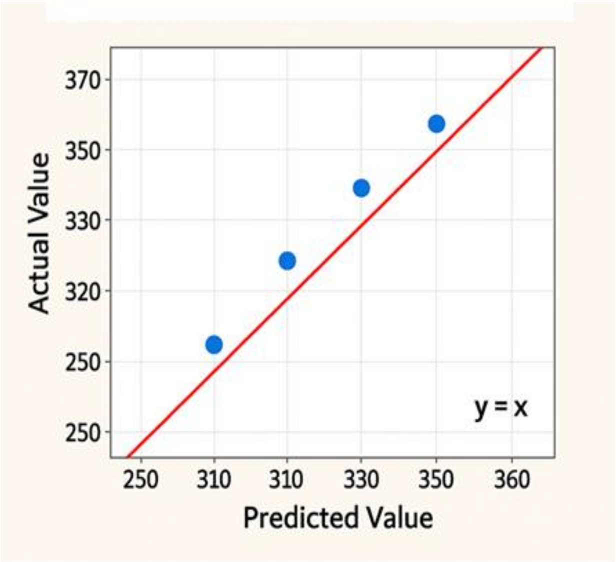

**Figure 13.** Actual with Predicted value

## Conclusion

The experimental investigation demonstrated that the addition of antioxidant additives, specifically Butylated Hydroxytoluene (BHT) and Ascorbic Acid, significantly influenced the performance and emission characteristics of Mahua biodiesel blends. Among the tested combinations, the B20 blend with optimal BHT and Ascorbic Acid concentrations showed improved brake thermal efficiency and reduced brake-specific fuel consumption compared to neat B20 fuel. The antioxidants effectively enhanced fuel oxidation stability, leading to a more complete combustion process and lower emissions of carbon monoxide (CO), unburned hydrocarbons (HC), and smoke opacity.

However, a marginal increase in NOx emission was observed due to higher combustion temperatures associated with improved oxidation. Optimization using response surface methodology (RSM) revealed that the additive concentrations played a critical role in achieving the best overall performance–emission trade-off. The desirability function analysis confirmed that the combined use of BHT and Ascorbic Acid in appropriate proportions yielded superior results compared to individual additive use.

Overall, Mahua biodiesel blended with optimized antioxidant additives can serve as a sustainable and efficient alternative fuel for compression ignition engines, offering improved performance characteristics and reduced harmful emissions without any major engine modification. Future studies may focus on long-term stability analysis and the interaction effects of combined antioxidants under varied engine operating conditions.

**Authors Contribution**
All authors have contributed equally to prepare the paper.

**Availability of data and materials**
The data that support the findings of this study are available from the corresponding author, upon reasonable request.

**Conflict of interests**
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.

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