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RESEARCH ARTICLE

Effects of Pre-Injection and Antioxidants in a Diesel Engine Fuelled with Methyl Esters of Waste Cooking Oil Biodiesel

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ABSTRACT - Diesel engines are significant contributors to air pollution, particularly through emissions of nitrogen oxides (NOx), smoke, and carbon monoxide (CO). Finding sustainable fuel alternatives and additives to reduce emissions without compromising engine performance is imperative for environmental and public health concerns. This study investigates the impact of adding tert-butylhydroquinone (TBHQ) antioxidants to blends containing 20% Methyl Esters of Waste Cooking Oil (20MEOWCO) and 80% diesel fuel in Modified Common Rail Diesel (MCRD) engines. The experiment involves adjusting the pilot fuel injection timing to 36°CA bTDC (before Top Dead Centre) and the main injection timing to 15°CA bTDC, with a Nozzle Opening Pressure (NOP) of 500 bar. Biodiesel is produced from used cooking oil using standard procedures and then mixed with diesel fuel. Various concentrations of TBHQ are added to the 20MEOWCO fuel blend for the experiment. The findings indicate that introducing TBHQ in concentrations of 250 ppm and 500 ppm to the 20MEOWCO fuel blend results in a notable reduction of Oxides of Nitrogen (NO_x) emission by 13% in MCRD engines. However, this reduction in emissions comes at the expense of increased specific fuel consumption, which is observed to rise by 2.1%. Furthermore, the study highlights a rise in smoke and carbon monoxide (CO) emissions by approximately 7–10% and 5-8%, respectively, under the experimental conditions. The results of this study suggest that the addition of TBHQ to 20MEOWCO blends holds promise for mitigating NOx emissions in MCRD engines.

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1.0 INTRODUCTION

Energy shortages and rubbish disposal are becoming more prevalent in today's fast-paced culture. Besides electricity, which has the highest demand for all energy sources, the world has potential resources to meet energy needs. There is a need to use new techniques to convert garbage into alternative fuel. In an emergency, making biodiesel using locally accessible waste cooking oil may be a suitable alternative. It is also meant to produce biodiesel in a particular location, depending on the available sources of raw materials. The case for switching to biodiesel instead of traditional fuel in an internal combustion engine is to minimize pollution, which is made stronger by this study. To identify non-fossil renewable fuels that will outperform conventional diesel engines in aspects of combustion characteristics, effectiveness, and emission levels. The main disadvantages of using biodiesel are increased Oxides of Nitrogen (NO_x) emissions and decreased engine performance. The effects on cylinder peak pressure NO_x emission, brake thermal efficiency, and specific fuel consumption (SFC) are evaluated based on constant injection pressure and time with various loads. Numerous studies also consider other pollutants, including water, free fatty acids, sterols, phospholipids, etc. These components lead to higher pour points, clouds, viscosities, flashpoints, and lower volatility. Vegetable oil is thicker than other oils, and hence, it burns less efficiently and produces more smoke with carbon residue. A few methods exist, such as pyrolysis, emulsification, and transesterification. Among these, transesterification is a practical method for generating biodiesel from vegetable oil and improving its diesel-like qualities. The increased Oxygen, Carbon monoxide (CO), Hydrocarbon (HC), and smoke in biodiesel enable significant emission reductions that benefit the environment. Studied the use of B20 to reduce NO_x emission levels from diesel engines. B20 makes much less smoke than diesel in single and triple-injection situations [1].

High heat conductivity, increased calorific value, and increased surface-to-volume ratio of nanoparticles are significant in studying biodiesel properties. The biodiesel test mixes with diesel were prepared in five distinct combinations. The fuel mixture showcased commendable braking thermal efficiency and lower brake-specific fuel consumption (BSFC), HC, and NO_x emissions [2]. The study examined the Influence of three antioxidants, specifically Di-Ethyl Amine (DEA), Pyridoxine Hydro Chloride (PHC), and Tertiary butyl hydroquinone (TBH), on the performance and emissions of a single-cylinder diesel engine fueled by mango seed methyl ester [3]**.** Pomelo oil (Citrus maxima) makes biodiesel, which is then treated with the synthetic antioxidant Tertiary butyl hydroquinone. It has been noted that as TBHQ concentration increases, so does brake-specific fuel consumption. Whether using TBHQ or not, the biodiesel does not affect brake power [4]. The TBHQ peak oxidation was observed at a carbon paste electrode (CPE). However, the oxidation peak current was noticeably stronger in low concentrations [5]. It was determined that the standard of

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TBHQ, being much more efficient than Butylated hydroxyanisole (BHA), particularly at lower concentrations, has an additive effect, making the combination of such antioxidants inappropriate for increasing oxidative stability [6]. The study unveiled that, with a base FIP (Fuel injection pump) of 40 MPa for WCO20, both BSFC and NO_x increased while Brake thermal efficiency (BTE) decreased. The physical characteristics of the WCO20 fuel blend, particularly its viscosity and volatility, adversely affected the engine performance [7].

TBHQ was previously added to biodiesel and surfactant to increase its dispersion and improve performance. According to the results, the combination of 100 ppm Polyglyceryl-4-isostearate, TBHQ, Sorbitan Monooleate, and Glycerol Monostearate produced consistent biodiesel dispersion over one week [8]. To enhance the durability of diesel, a substantial number of various antioxidants, such as Butylated hydroxytoluene (BHT), pyrogallol (PY), and TBHQ, were introduced into waste cooking biodiesel [9]. Propyl Gallate, ButylatedHydroxy Toluene, Pyrogallol, and Tert-Butyl-Hydroquinone were the four synthetic antioxidants chosen for their oxidation stability (TBHQ). For testing, the performances of the specific TBHQ concentrations were added to biodiesel samples in the second stage [10]. The oxidative stability of biodiesel fuel derived from soybean oil meets the 6-hour first-class standard when TBHQ is utilized with biodiesel fuel [11]. Experimentally investigated the intricate impact of exhaust gas recirculation (EGR) on emissions, performance, and combustion and explored the energy characteristics of common rail direct injection (CRDI) engines fueled by diesel blends and waste fat sourced from the leather industry [12].

Experiments were conducted using different concentrations of antioxidants for Eucalyptus biofuel blends (100, 250, 500, and 1000 ppm). The findings suggest that PHC is decreasing NO_x production [13]. The study examines the effects of TBHQ antioxidant addition doses on Calophylluminophyllum biodiesel's thermal balance, enhanced oxidation balance, and long-term garage balance. It is concluded that Calophylluminophyllum biodiesel can be kept fresh for a long period by treating it with 1000 ppm of the antioxidant TBHQ [14] The study aimed to investigate the compatibility of a newly developed tamarind seed methyl ester (TSME) and its interaction with the different concentrations of antioxidant additive butylated hydroxyanisole, including 1000 and 2000 ppm additions [15]. The effectiveness of antioxidants based entirely on fragrant amines in improving the oxidation balance of biodiesel and lowering nitrogen oxides in tailpipe emissions was studied. The feedstock for biodiesel synthesis was vegetable oil from the Calophylluminophyllum genus, and TBHQ was used as an antioxidant. The results showed that biodiesel blended fuels had a 3% to 10% lower BTE than the baseline [16]. The performance of compression ignition (CI) engines fueled by blends of hemp-derived biodiesel, diesel, and a TBHQ additive was evaluated by testing the diesel and S20 [17]. Biodiesel features changed under severe oxidation when biodiesel from various sources, such as cardoon, leftover cooking oil, high-oleic sunflower oil, and rapeseed oil, were used. Compared to high-oleic safflower, cardoon, and waste cooking oil (WCO) biodiesel needed more concentrations of TBHQ [18]. Blending low-viscosity biofuel (wintergreen oil) with diesel results in an effective replacement fuel that starts with enhanced BTE and a drop in carbon dioxide (CO_2) emissions and other pollutants [19]. Through focusing on additional diesel and biodiesel additives, reductions of approximately 75% and 100% were achieved for CO, HC, soot, and NO_x, with percentages of 65% and 75%, 60% and 75%, and approximately 25% and 45%, respectively. Furthermore, compared to diesel, there was an increase of around 6% and 15% in the maximum flame temperature, respectively [20].

A single-cylinder engine operating at 2400 rpm and 60% load was used to test the effects of biodiesel at levels of 20% and 40% by volume to a mixture of diesel (70%) and isopropanol-butanol-ethanol (30%) on engine performance. The findings indicated a minor rise in smoke darkness and CO and reduced HC and NO_x emissions [21]. The results of varying fuel injection methods on a CRDI engine at various loads were investigated using a 20% biodiesel mixture of TSME. A 30% pilot injection of TSME biodiesel is usually advised as an alternative gasoline for diesel engines because it performs better and emits fewer pollutants [22]. It was concluded that using these micro-emulsions and an optimized injection strategy can reduce NO_x and particulate matter emissions in a CRDI engine [23] The CRDI car diesel engine chosen for this examination has an electronically managed gas injection gadget that allows it to adjust single and multiple injection schedules in addition to gas injection pressure. The test outcomes proved that the emissions of a waste-cooking biodiesel blend could be appreciably decreased by using a pilot and post-injection pressure [24].

The results revealed that the higher proportion of ethanol in the blends led to an increased corrosion rate. Additionally, including ethanol diminished TBHQ's efficacy in preventing corrosion [25]. The optimization of injection settings of CRDI engines that run on 80% diesel and 20% waste lemon peel oil is studied to enhance performance and decrease emissions. The essential diesel injection settings enhance efficiency and minimize pollutants [26]. It presents an analysis examining how variable compression ratio (VCR) diesel engine performed, what kind of pollution it produced, and how well it burned non-edible biodiesel. The engine was tested with three distinct compression ratios, running at 1500 rpm and 300 psi of injection pressure [27] For the engine tests, different engine loads and speeds were employed; according to the findings, using ternary fuel reduced heat efficiency by about 7% while increasing brake fuel consumption by nearly 18%. The findings show that CO_2 emissions from the test fuels were comparable between petrol and diesel emissions [28]. An experiment tested the engine and various injection timings (23, 25, and 27° bTDC) with different fuel injection pressures to optimize the injection settings (20, 35, and 500 bar). The split injection combustion approach has been studied under optimal fuel injection conditions [29]. It was revealed by the research that the addition of antioxidants incompatible with moist or humid storage conditions accelerates the loss of stability beyond expectations. This issue can be mitigated by opting for nonpolar compounds [30].

A CRDI engine that ran on Karanja biodiesel blends rather than conventional diesel. The particle number concentration peaked when the biodiesel proportion of the blended test gasoline reached 10%, and it then continued to rise. Biodiesel was injected in very small amounts into the test fuel to reduce particle emissions [31]. The engine was evaluated while the nozzle was opened to its ideal pressure of 500 bar. The injection time is varied, and the post-injection time is gradually adjusted; alternative theoretical and empirical models, in particular, are typically preferred over artificial neural networks. Unlike biodiesel-powered engines, multiple injection strategies significantly reduced emissions while improving performance [32]. To assess how diesel engine injection techniques, affect particle size-number distributions, extent awareness distributions, floor area, and the timing at which the engines begin to inject fuel. Four distinct injection times and three excellent diesel engine injection pressures with 300, 500, and 750 bars have been investigated [33]. Research work investigated the combustion and emission performance by pollution of a variable compression ratio (VCR) diesel engine fed with n-butanol blends fuel [34].

A CRDI engine was used to run the aggregate of biodiesel obtained from plants and animals. The combinations B25, B50, and B75 were developed in the lab using diesel and swine lard methyl esters and a bio-component single-step alkali transesterification system [35]. The pilot and main injection timings changed when testing an engine with various injection pressures (500 and 1000 bar). The percentage of gasoline utilized, especially for BSFC, rose with the addition of Karanja biodiesel to test fuels [36]. The method presented highlights the promise of subabul seed biodiesel as a workable alternative for diesel engines. Crude oil was recovered by mechanically crushing the subabul seeds. Subsequently, Subabul seed methyl ester 10 (SSME 10), SSME 20, and SSME 30 biodiesel blends were created based on volume, and the engine performances were tested [37]. The study focused on converting dairy waste into biodiesel and evaluating the Impact of antioxidants on stability. The biodiesel induction period (IP) was notably extended with the addition of an antioxidant (TBHQ) [38]. Timing, speed, and split injection are all managed at various injection pressures under the direction of an open-type electronic control unit. The data analysis indicates that injection pressure and time significantly impact combustion characteristics when the parameters are constant [39].

This investigation was done by operating an MCRD diesel engine at full load with a B20 mixture of neat diesel (80%) and MEOWCO (20%), along with TBHQ (antioxidant), and timing of the pilot injection while maintaining a constant pilot injection pressure of 500 bar at 36°CA TDC. In this work, TBHQ is chosen as an antioxidant. TBHQ is a potent antioxidant that can hinder free radical formation and prevent lipid oxidation, a critical factor in upholding biodiesel stability. Its role in minimizing oxidation extends biodiesel's shelf life and storage stability, which are derived from waste cooking oil. The findings indicated that when 1 gm of pilot fuel was mixed with TBHQ additive and without TBHQ additive at an injection pressure of 500 bar, the antioxidant concentrations of 250 ppm and 500 ppm were added. The main injection time was 15°CA bTDC, and the pilot injection time was 36°CA bTDC. This study aims to reduce the amount of pollutants that an engine releases.

2.0 SETUP FOR AN EXPERIMENT

Experiments were conducted using a water-cooled, 3.5 kW single-cylinder Modified Common Rail Diesel (MCRD) engine, operating under 75% and 100% constant loads. The engine, equipped with ECU and software, allowed for adjustable injection pressure. A B20 fuel blend was used, comprising 80% pure diesel and 20% biodiesel from MEOWCO. The engine maintained a consistent PI timing of 36°CA bTDC and MI timing at 15°CA bTDC (15M), both with a NOP of 500 bar. TBHQ antioxidant was added to the MEOWCO fuel. Tables 1 and 2 detail the properties of diesel and biodiesel, while Table 3 provides information on TBHQ properties. Figure 1 displays the results obtained from the experimental testing setup, and Figure 2 illustrates the schematic diagram of the setup.

The intentional timing difference at this level aimed to allow sufficient time for effectively mixing fuel and air under the specified load conditions. A Five Gas Analyzer measured CO, NO_x, and HC. The analyzer's range covered HC measurements from 0 to 20,000 ppm, CO from 0% to 20% by volume, and NO_x from 0 to 5000 ppm. The engine exhaust gas temperature was monitored using a K-type thermocouple with a digital display. The AVL 365C Encoder was used to measure the crank angle, and an open electronic control unit (ECU) Engine- with a soft software system was used to gather information from the pressure sensor, crank angle encoder, injection time, and pressure. A detailed investigation of many engine performance characteristics and emissions under varied running situations was made possible by this extensive experimental setup.

The necessary data is collected from the received signals through processing, including parameters such as the heat release rate, ignition delay, etc.

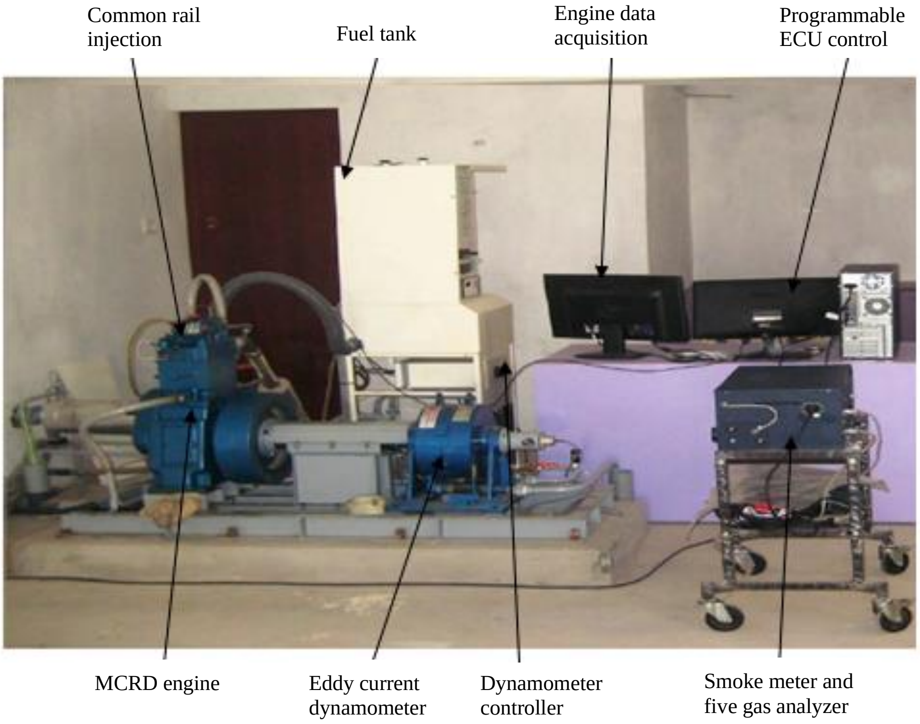
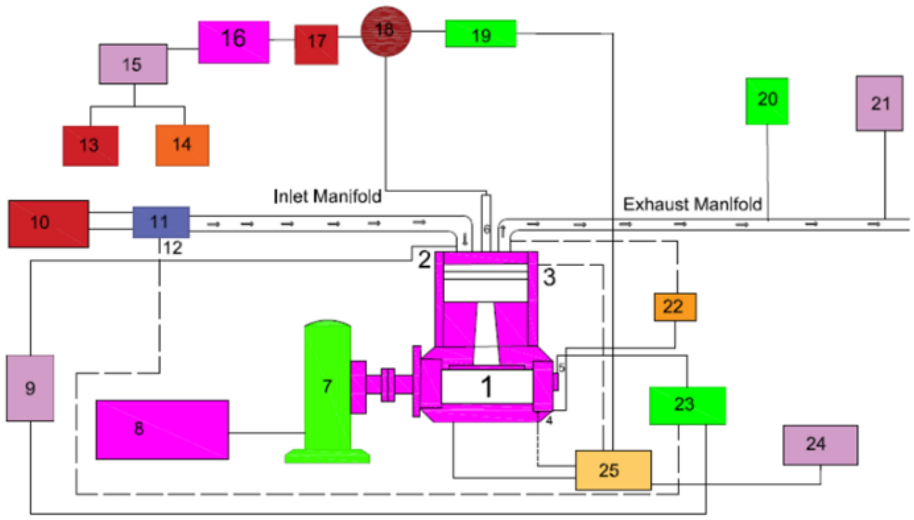


Figure 1. Experimental setup



1. MCRD Engine
2. Pressure Sensor
3. Coolant Temperature Sensor
4. Cam Sensor
5. Crank Angle Sensor
6. Solenoid Injector
7. Eddy Current Dynamometer
8. Dynamometer Controller
9. Charge Amplifier
10. Surge Tank
11. Air Flow Meter
12. Air Flow Sensor
13. Diesel Tank
14. Biodiesel
15. Fuel pump
16. Fuel Measuring Unit
17. Fuel Filter
18. High-pressure fuel pump
19. Common rail
20. Exhaust gas analyser
21. Smoke meter
22. Combustion analyser
23. Data Acquisition system
24. Programmable ECU controller
25. A-D Converter

Figure 2. Experimental setup schematic diagram

Table 1. Properties of diesel and biodiesel

ASTM Norms	Diesel	Biodiesel (MEOWCO+Diesel)	Properties
ASTM D1298	860	873	Density at 16 ºC (kg/m^3)
ASTM D445	3.2	4.15	Kinematic viscosity at 40 ºC (cSt)
ASTM D93	75	184	Flash Point (ºC)
ASTM D2500	18	15.5	Cloud Point (ºC)
ASTM D613	49	51	Cetane number
ASTM D240	43.0	38.012	Calorific value (MJ/kg)
ASTM D130	3.1	2.4	Copper strip corrosion
EN14214	-	19.0	Iodine value (I2/100 g)
ASTM D6584	-	41.1	Palmitic (C10.0) (% weight)
ASTM D6584	-	4.4	Stearic (C18.0) (% weight)
ASTM D6584	-	41.9	Oleic (C18.1) (% weight)
ASTM D6584	-	9.6	Linoleic (C18.2) (% weight)
ASTM D6584	-	0.49	Linolenic (C18.3) (% weight)

Table 2. Details of the test engine specification

Parameters	Specifications
Engine model	Kirloskar
Type of engine	Four strokes and single-cylinder diesel engine at a constant speed
Capacity	660cc
Engine bore and stroke length	87.5 mm x 110 mm
Machine programmable ECU	Model Nira (solenoid injector)
Variable compression ratio	12 to 18
Speed	1500 ~1600 rev/min
Power rate	3.5 kW
Nature of the loading	Eddy current dynamometer
Changes in injection pressure	200 bar-800bar
Changing in injection timing	29º~15ºbTDC
Temperature Sensor	K-Type Thermocouple

Table 3. Properties of the TBHQ

Properties	TBHQ
Molecular Formula	$C_{10}H_{14}O_2$
CAS Number	1948-33-0
Molecular Weight	166.221 g / mol
Melting point	127-129 °C (lit.)
Boiling point	273 °C
Density	1050 kg/m^3
Vapor pressure	0.004 Pa at 25°C
Flash point	171 °C

3.0 RESULTS AND DISCUSSION

This research project used Methyl esters of waste cooking oil (20MEOWCO) as fuel in an MCRD engine. As an antioxidant, different concentrations of TBHQ (between 250 and 500 ppm) were mixed into the gasoline. The main injection timing was set at 15°CA bTDC with a normal operating pressure (NOP) of 500 bar, and the pilot injection timing was consistently maintained at 36°CA bTDC throughout the research. The study concentrated on several important factors: smoke, CO, HC and NO_x emissions, cylinder pressure, heat release rate (HRR) and SFC.

3.1 Variation of Cylinder Pressure

In general, an increase in peak cylinder pressure indicates more engine vibrations, loss in fuel efficiency, and high NO_x production. Figures 3 and 4 show the in-cylinder pressure with a crank angle for diesel, 20MEOWCO, 20MEOWCO+TBHQ (250ppm), and 20MEOWCO+TBHQ (500ppm) at higher loads (75% and 100% load). 75% and 100% load conditions for HRR and cylinder pressure were discussed in this article, as most of the engines operate at part load and full condition only. Using 20MEOWCO without TBHQ results in a discernible but marginal increase in cylinder pressure. This phenomenon is attributed to a lower ignition delay associated with using 20MEOWCO. The study notes that biodiesel, in this context, displays a shorter ignition delay than conventional diesel despite possessing higher viscosity and lower volatility. This observation suggests that the heightened cetane number of the biodiesel used may contribute to the reduced ignition delay, thereby influencing the combustion process.

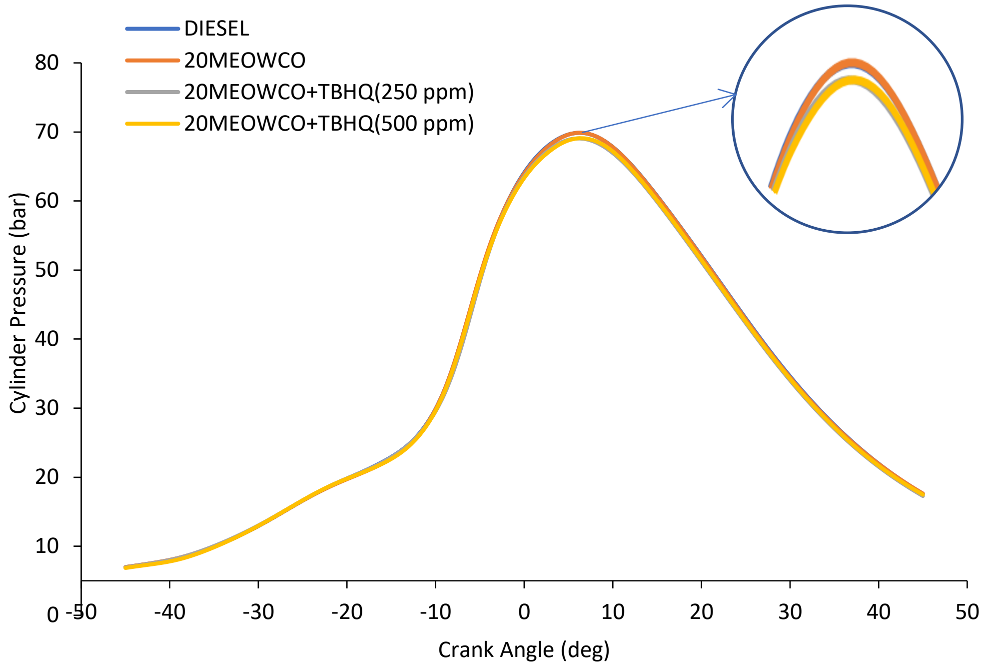


Figure 3. Cylinder pressure vs crank angle at 75% load, 500 bar-15º bTDC main injection / 36º bTDC pilot injection

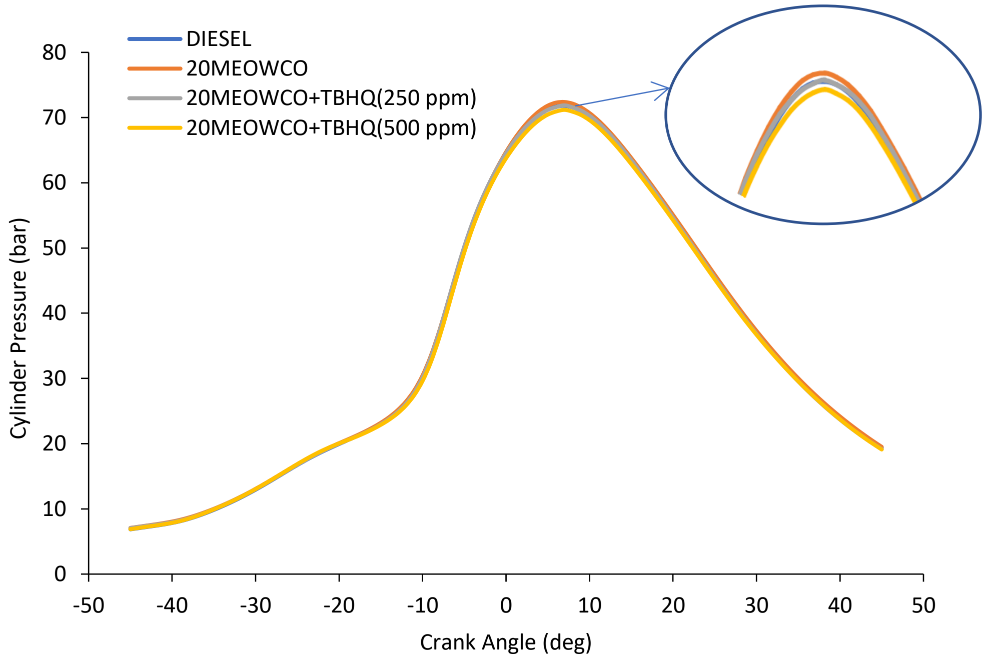


Figure 4. Cylinder pressure vs crank angle at 100% load, 500 bar-15º bTDC main injection / 36º bTDC pilot injection

Peak cylinder pressure at full engine load was 71.8 bar for diesel, 72.38 bar for 20MEOWCO, 71.24 bar for 20MEOWCO+TBHQ (250ppm), and 71.08 bar for 20MEOWCO+TBHQ (500 ppm). It was concluded that 20MEOWCO + TBHQ (500 ppm) has a lower in-cylinder pressure, and 20MEOWCO blends without antioxidants have a higher in-cylinder pressure than other fuels. The higher peak pressure of 20MEOWCO fuel may be due to higher fuel-bound molecular oxygen and cetane than conventional diesel. Interestingly, the research indicates that by raising the concentration of TBHQ in the 20MEOWCO blend, peak combustion pressure decreases. This reduction is attributed to the production of higher radical scavenger molecules facilitated by TBHQ. The scavenger molecules are instrumental in minimizing the oxidation of fatty acid methyl esters within the 20MEOWCO fuel. By acting as antioxidants, TBHQ molecules counteract the formation of free radicals during combustion, thereby mitigating oxidative processes and lowering the peak combustion pressure.

3.2 Variation of Heat Release Rate

In Figures 5 and 6, the graphical representations illustrate the variations in HRR and crank angle for various fuels: diesel, 20MEOWCO, 20MEOWCO+TBHQ (250ppm), and 20MEOWCO+TBHQ (500ppm) under higher load conditions (75% and 100% load. It is crucial to understand that the production of NO_x is intricately linked to the peak combustion temperature, a parameter directly influenced by the peak HRR throughout the combustion process. A lower HRR is deemed advantageous as it corresponds to a more gradual and controlled release of energy during combustion. This controlled release is beneficial for minimizing the combustion temperature, subsequently taking the lead to lower production of NO_x.

It is observed that HRR is higher for 20MEOWCO and lowest for 20MEOWCO+TBHQ (500ppm) compared to conventional diesel fuel. The heightened peak pressure in 20MEOWCO fuel can be attributed to fuel-bound oxygen and the higher cetane number of biodiesel utilized. A rise in the concentration of TBHQ with 20MEOWCO results in a noticeable reduction in peak HRR.

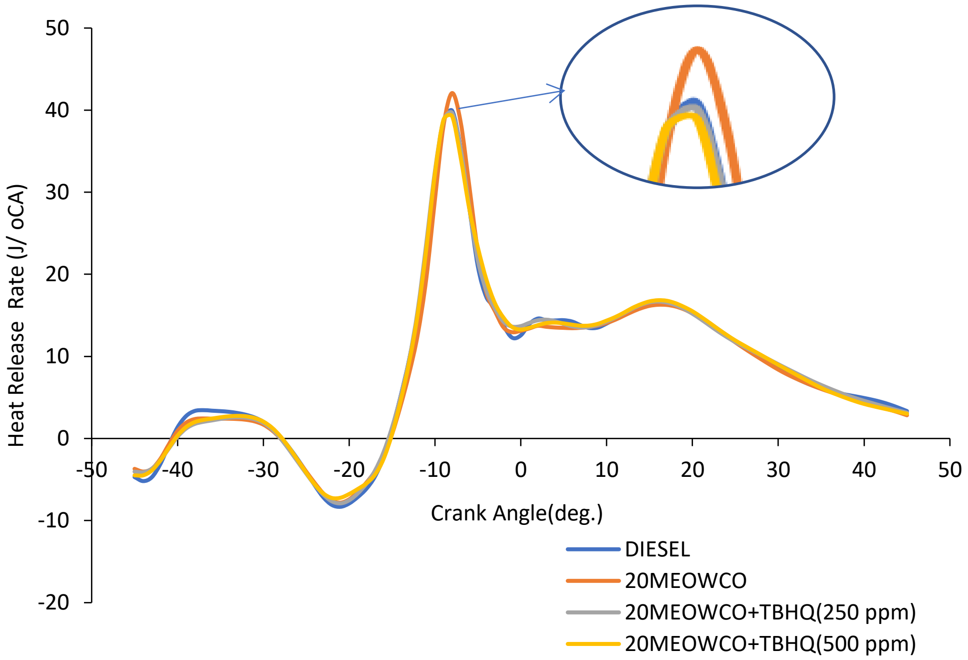


Figure 5. Heat release rate vs crank angle at 75% load, 500 bar-15º bTDC main injection / 36º bTDC pilot injection

When the injection was performed using 20MEOWCO as planned, two unfavorable patterns in heat release were observed. These two negative values will greatly reduce the maximum heat emitted during combustion. Due to the pilot mode's early fuel injection and accompanying explosion, the diesel will vaporize quickly during the main injection event. Because of the pilot mode's early fuel infusion and the explosion that followed, which decreases the physical delay of the fuel and raises the total heat release rate, the diesel will vaporize quickly during the main injection event. Various quantities of antioxidants, such as TBHQ (250 ppm) and TBHQ (500 ppm), slow the rate at which heat is released. The 20MEOWCO biodiesel additionally increases the cetane index of biodiesel. It can reduce waiting time and hasten the fuel's subsequent combustion.

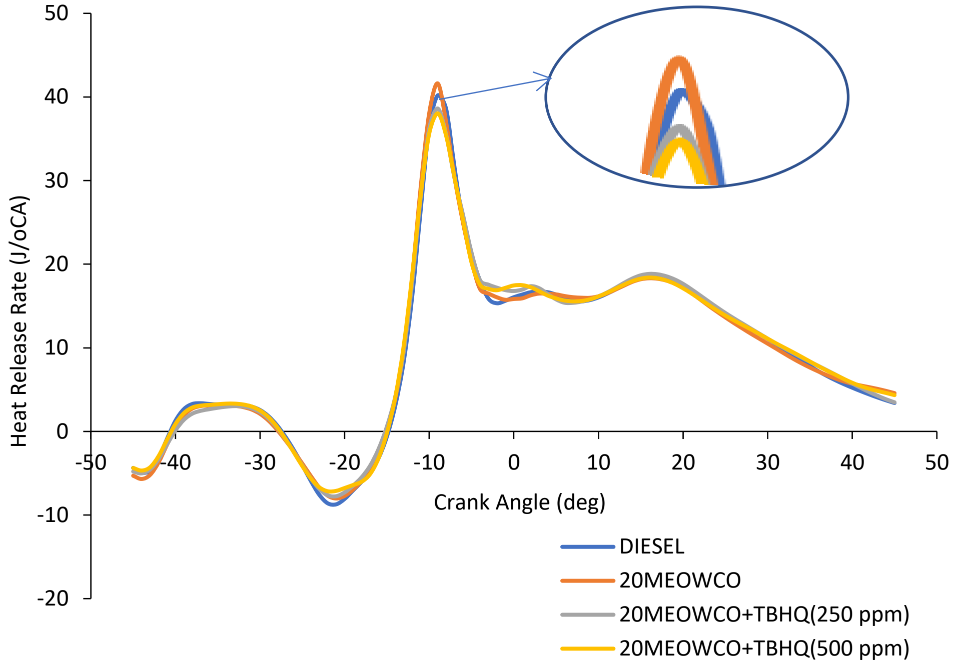


Figure 6. Heat release rate vs crank angle at 100% load, 500 bar-15º bTDC main injection / 36º bTDC pilot injection

3.3 Comparison of Specific Fuel Consumption

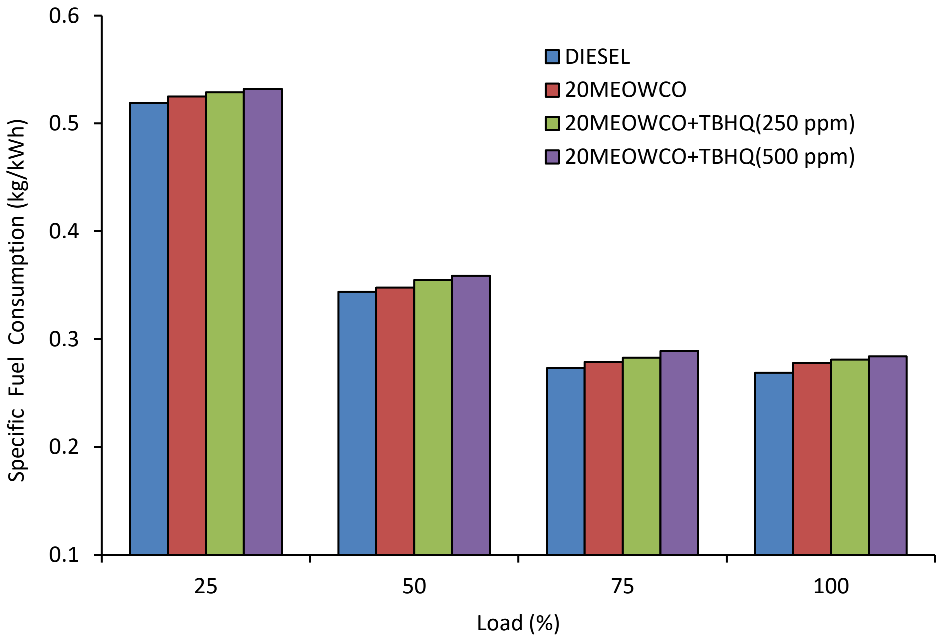


Figure 7. Specific fuel consumption vs load, 500 bar-15º bTDC main injection / 36º bTDC pilot injection

Specific fuel consumption is used to measure engine performance since it demonstrates how much diesel is required to produce one unit of braking power. Variances in specific fuel consumption were observed for 20MEOWCO fuel with and without antioxidants across different loads in the MCRD engine.

In Figure 7, a comparison of specific fuel consumption (SFC) at rated power shows that the 20MEOWCO fuel has an increased SFC of 0.278 kg/kWh compared to conventional diesel with an SFC of 0.269 kg/kWh. Suggests that the 20MEOWCO biodiesel blend requires marginally increased fuel use to generate a similar strength as conventional diesel fuel. The higher SFC for 20MEOWCO is attributed to its lower calorific value, higher viscosity, and higher molecular weight hydrocarbons, collectively resulting in a less energy-dense fuel. Additionally, the analysis indicates that the SFC further rises as the concentration of TBHQ (tert-butylhydroquinone) in the 20MEOWCO blend increases. The highest SFC is observed for the 20MEOWCO+TBHQ (500ppm) blend, reaching 0.280 kg/kWh at rated power. The increase in SFC with the addition of TBHQ suggests that the antioxidant influences combustion dynamics, affecting the consumption of fuel per unit of power produced. The observed trend indicates that as the percentage of TBHQ increases, the combustion rate decreases, leading to higher specific fuel consumption.

3.4 Variation of Smoke Emission

Figure 8 visually depicts variations in smoke levels for different fuels (diesel, 20MEOWCO, 20MEOWCO+TBHQ (250ppm), and 20MEOWCO+TBHQ (500ppm)) across all load conditions in the MCDR engine. Smoke generation during combustion is intricately linked to oxygen concentration. The graph reveals a significant and noteworthy 3.8% reduction in smoke levels for the 20MEOWCO fuel compared to conventional diesel. This decrease is primarily associated with the elevated O_2 content in the 20MEOWCO biodiesel blend, promoting a more thorough and efficient combustion process and decreasing smoke emissions.

The examination showed that incorporating concentrations of 250 ppm and 500 ppm of TBHQ into the 20MEOWCO fuel led to a respective 7.5% and 10.1% escalation in smoke compared to the 20MEOWCO fuel alone. This phenomenon is ascribed to the heightened presence of C-C bonds and increased aromatic material induced by including antioxidants. These changes in chemical composition are believed to contribute to the observed elevation in smoke levels.

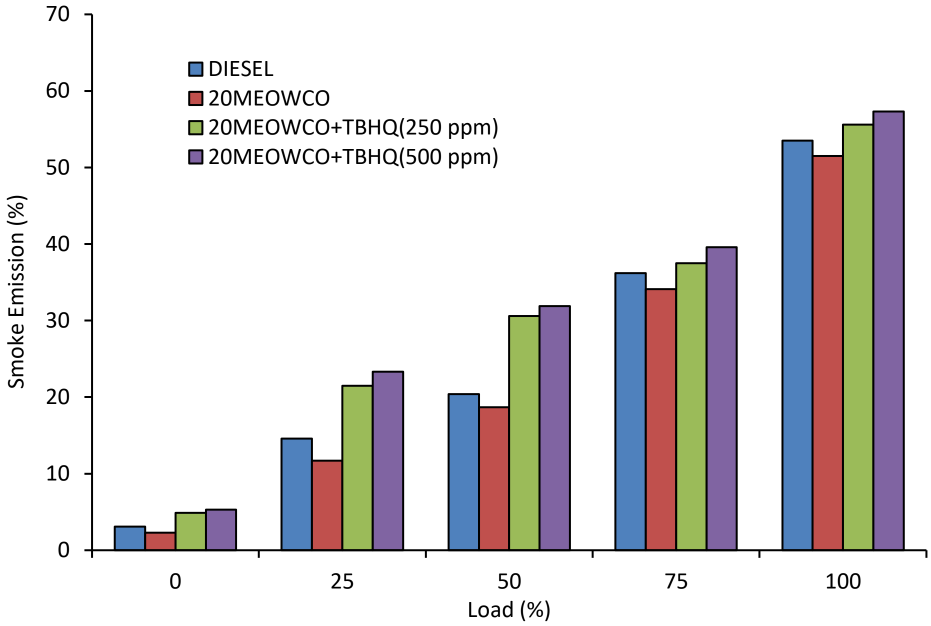


Figure 8. Smoke emission vs load, 500 bar- 15° bTDC main injection / 36° bTDC pilot injection

3.5 Variation of Oxides of Nitrogen Emission

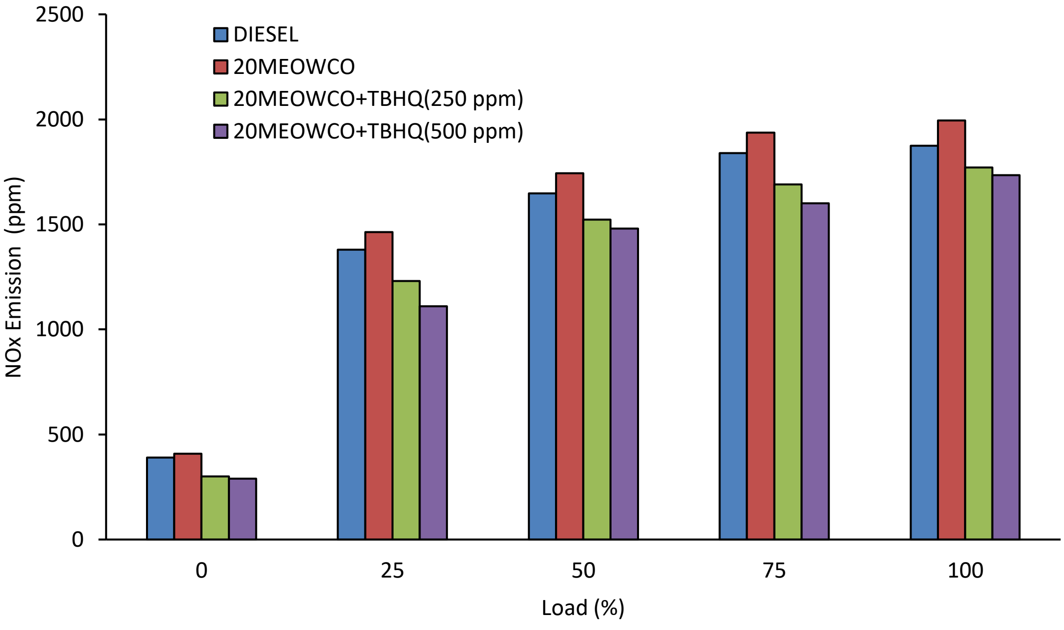


Figure 9. NO_x emission vs load, 500 bar-15° bTDC main injection / 36° bTDC pilot injection

Figure 9 shows the effect of TBHQ (0, 250 ppm, 500 ppm) as an antioxidant on NO_x emission with the percentage of load for 20MEOWCO fuel in the MCRD Engine. With 20MEOWCO fuel, NO_x emissions are elevated at all loads compared to diesel fuel. A maximum of 120 ppm increase is found at the rated power of the MCRD engine for 20MEOWCO fuel. This may be due to fuel-bound oxygen in 20MEOWCO, higher adiabatic combustion temperature, the higher cetane number of 20MEOWCO, formation of CH radicals, and larger droplet size due to higher viscosity. The study reveals that tert-butylhydroquinone (TBHQ) decreases NO_x when combined with the 20MEOWCO fuel, surpassing the performance observed with conventional diesel across all loads. The rise in TBHQ concentration in the B20 fuel correlates with a consistent decrease in NO_x. Notably, the maximum decrease in NO_x reached 11.1% with the addition of 250 ppm of TBHQ, and a further improvement was achieved with 500 ppm, resulting in a 13% reduction with the 20MEOWCO fuel. This observation indicates the potential for fine-tuning the TBHQ concentration to achieve optimal NO_x reduction while using 20MEOWCO as a biodiesel blend. The achieved reductions, with a maximum of 13% at 500 ppm TBHQ addition, signify the promising role of TBHQ as an effective additive for NO_x emission control in biodiesel-fueled engines.

The radical scavenger molecule will be strengthened by adding TBHQ molecules as antioxidants in the 20MEOWCO fuel, which will also stop the fatty acid methyl esters of biodiesel from oxidizing, which is the cause of the reduction in NO_x. A benzene ring is joined to two hydroxyl groups in the phenolic molecule known as TBHQ. Due to their reactivity as a hydrogen or electron-donating agent from the hydroxyl group to the chain-carrying free radicals, phenolic compounds are known to have the property to reduce the oxidation rates of organic matter. This property is necessary to stop the chain propagation step during the oxidation process.

3.6 Variation of Carbon Monoxide Emission

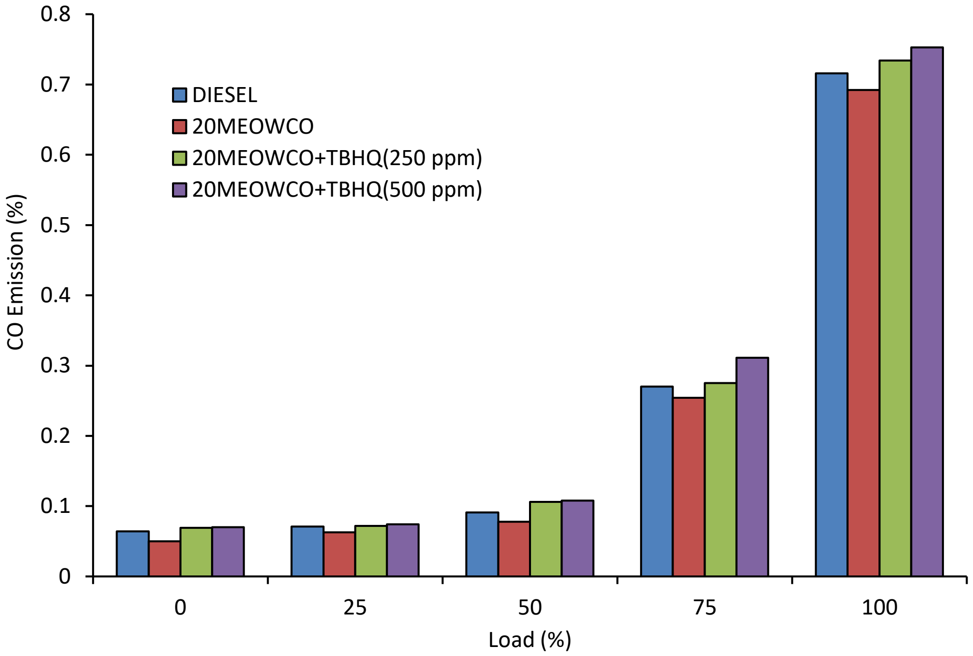


Figure 10. CO emission vs load, 500 bar- 15º bTDC main injection / 36º bTDC pilot injection

Figure 10 shows the variations in carbon monoxide for diesel, 20MEOWCO, 20MEOWCO+TBHQ (250ppm), and 20MEOWCO+TBHQ (500ppm) at all loads in the MCRD engine. Figure 10 illustrates the growth in CO emission with the rise in loads and highest at rated power under all tested circumstances.

The observed trend in increased CO emissions with the addition of antioxidants, specifically tert-butylhydroquinone (TBHQ), to the 20MEOWCO fuel can be attributed to several factors. One contributing factor is the fuel's tendency to become relatively richer at higher loads, leading to more fuel-rich zones during combustion. This shift in combustion characteristics may result in increased CO emissions, as incomplete combustion in fuel-rich regions can lead to the generation of carbon monoxide. Interestingly, when considering CO emissions alone, the 20MEOWCO biodiesel fuel demonstrates greater efficiency than conventional diesel. Because biodiesel has a higher oxygen content, it burns more efficiently and emits less CO. This improved efficiency results from this. However, a counterintuitive increase in CO emissions is observed when antioxidants like TBHQ are introduced into the 20MEOWCO fuel. Specifically, at maximum load, the CO emissions were determined to increase by 5.72% and 8.1% for 20MEOWCO+TBHQ (250ppm) and 20MEOWCO+TBHQ (500ppm), respectively, in comparison with the 20MEOWCO fuel alone. The introduction of antioxidants, such as TBHQ, into the fuel blend has the effect of lowering peroxyl and hydrogen peroxide radicals, which are known to hurt the generation of hydroxyl radicals and the oxidation of CO. This deduction in radical species, intended to enhance combustion stability, inadvertently leads to increased CO emissions.

3.7 Variation of Hydrocarbon Emission

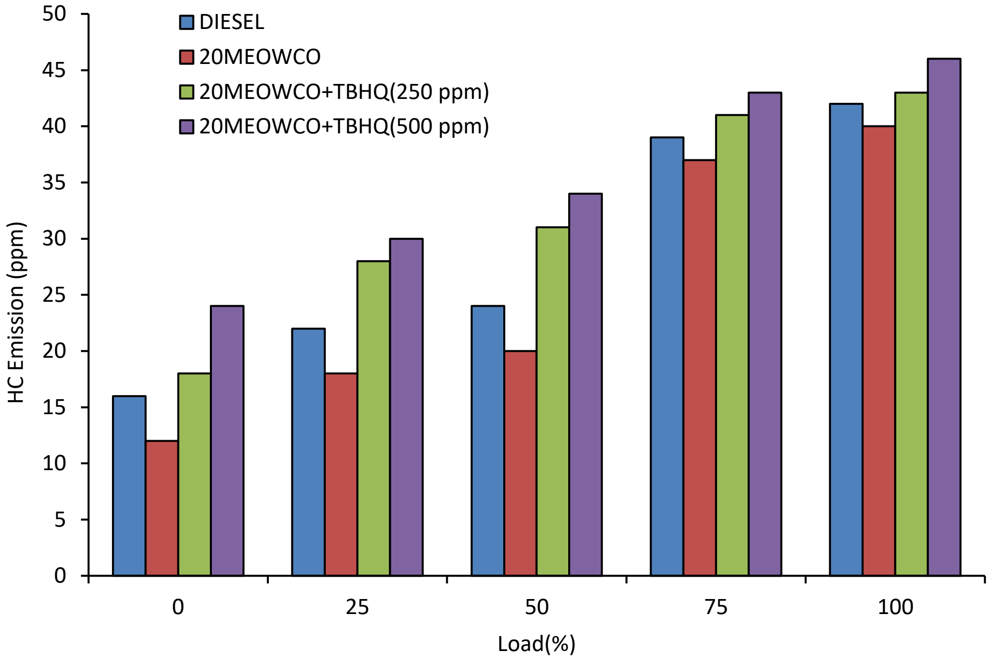


Figure 11. HC emission vs load,500 bar-15° bTDC main injection / 36° bTDC pilot injection

Hydrocarbon (HC) emissions originate from a variety of combustion process components. One of the main causes of the problem is incomplete combustion, which occurs when certain fuel molecules do not combine with oxygen to form carbon dioxide and water. This incomplete combustion results in the release of unburned hydrocarbons into the exhaust gases. The air-fuel mixture's composition also plays a pivotal role in HC emissions. Excessive lean (insufficient fuel relative to air) and overly rich (excessive fuel relative to air) mixtures can contribute to higher HC emissions.

The variations in carbon monoxide levels in the MCRD engine at all loads for diesel, 20MEOWCO, 20MEOWCO+TBHQ (250ppm), and 20MEOWCO+TBHQ (500ppm) are shown in Figure 11. When 20MEOWCO fuel is used instead of pure diesel, there are fewer hydrocarbon (HC) emissions. This HC could be because biodiesel fuels have a greater molecular oxygen concentration, which ensures full combustion. In comparison to 20MEOWCO fuel under maximum load circumstances, Figure 11 shows that the addition of antioxidant TBHQ (250 ppm) and TBHQ (500 ppm) with 20MEOWCO fuel, at the same injection pressure and timing, increases HC emissions by 3 ppm and 6 ppm, respectively. The primary cause of the rise in HC emissions has been mitigated by the addition of antioxidants, which have decreased the production of free radicals.

4.0 CONCLUSIONS

This research aimed to evaluate the CO, HC, smoke, and NO_x emissions by optimizing the pilot injection strategy from an MCRD engine running with a mixture of TBHQ and 20MEOWCO. The results showed that adding TBHQ as an antioxidant had a noticeable impact on the engine's emissions. In particular, the study investigated how cylinder pressure, HRR, SFC, and BTE affected the emissions of CO, HC, smoke, and NO_x during combustion. The following summarizes the study's key findings:

a) The Impact of increasing tert-butylhydroquinone (TBHQ) concentration from 250 ppm to 500 ppm in 20MEOWCO fuel reveals a reduction in cylinder peak pressure and HRR. It indicates that higher concentrations of TBHQ lead to a reduction in cylinder peak pressure. It suggests a more controlled and less forceful expansion of gases within the cylinder.

b) The SFC increases when 500 ppm of TBHQ antioxidant is added. In conclusion, there is a 1.14% decrease in brake thermal efficiency.

c) The observed 13% reduction in nitrogen oxide (NO_x) emissions, achieved by increasing TBHQ from 250 ppm to 500 ppm, highlights the potential of this antioxidant to mitigate a major contributor to air pollution effectively. This finding suggests that higher concentrations of TBHQ contribute to a more controlled combustion process, leading to reduced NO_x emissions.

d) A discernible 11% increase in hydrocarbon (HC) emissions and a 10% increase in smoke emissions were observed.

e) The investigation showed that adding 500 ppm of TBHQ with 20MEOWCO would considerably reduce NO_x emissions while slightly increasing HC, CO, and smoke emissions without affecting engine performance.

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6.0 REFERENCES

[1] N. Chacko, S. Rajkumar, and J. Thangaraja, “Experimental and modeling analysis of multiple-injection strategies with B20 operation in a CRDI engine,” *Fuel,* vol. 293, p.120433, 2021.

[2] S. N. K. Reddy and M. M. Wani, “An investigation on the performance and emission studies on diesel engine by addition of nanoparticles and antioxidants as additives in biodiesel blends,” *International Review of Applied Sciences and Engineering,* vol. 12, no. 2, pp. 111–118, 2021.

[3] K. Velmurugan and A. P. Sathiyagnanam, “Impact of antioxidants on NOx emissions from a mango seed biodiesel powered di diesel engine,” *Alexandria Engineering Journal*, vol. 55, no. 1, pp. 715–722, Mar. 2016.

[4] M. Saikia, K. Bora, and K. Kalita, “Effect of TBHQ on the Combustion Characteristics of Pomelo oil Biodiesel in a Compression Ignition Engine,” *Journal of Scientific & Industrial Research*, vol. 79, pp. 81-83, 2020.

[5] T. A. de Araújo, A. M. J. Barbosa, L. H. Viana, and V. S. Ferreira, “Voltammetric determination of tert-butylhydroquinone in biodiesel using a carbon paste electrode in the presence of surfactant,” *Colloids and Surfaces B: Biointerfaces*, vol. 79, no. 2, pp. 409–414, 2010.

[6] S. Nogales-Delgado, J. M. Encinar, and J. F. González, “Safflower biodiesel: Improvement of its oxidative stability by using BHA and TBHQ,” *Energies (Basel),* vol. 12, no. 10, p.1940, 2019.

[7] S. K. Gugulothu, B. Deepanraj, R. V. Reddy, and L. S. Sundar, “Influence of split injection strategies and Trade-off study on the CRDI engine characteristics powered with waste cooking Oil/Diesel blend,” *Fuel*, vol. 344, p. 128023, 2023.

[8] H. Sutanto, B. H. Susanto, and M. Nasikin, “The Effect of Surfactant Addition towards Dispersion and Antioxidant Activity of tert-butylhydroquinone in Biodiesel,” ”*International Journal of Renewable Energy Research,* vol.8, no.4 , pp. 1974-1979, 2018.

[9] G. Uğuz, A. E. Atabani, M. N. Mohammed, S. Shobana, S. Uğuz, G. Kumar, and H. Ala'a, “Fuel stability of biodiesel from waste cooking oil: A comparative evaluation with various antioxidants using FT-IR and DSC techniques,” *Biocatal Agric Biotechnol*, vol. 21, pp. 101283, 2019.

[10] S. Rajamohan, A. H. Gopal, K. R. Muralidhara, Z. Huang, B. Paramasivam, and T. Ayyasam, “Evaluation of oxidation stability and engine behaviors operated by Prosopis juliflora biodiesel/diesel fuel blends with presence of synthetic antioxidant,” *Sustainable Energy Technologies and Assessments*, vol. 52, p. 102086, 2022.

[11] K. Ryu, “The characteristics of performance and exhaust emissions of a diesel engine using a biodiesel with antioxidants,” *Bioresour Technology,* vol. 101, no. 1, Supplement, pp. S78–S82, 2010.

[12] T. Esakki, S. M. Rangaswamy, and R. Jayabal, “An experimental study on biodiesel production and impact of EGR in a CRDI diesel engine propelled with leather industry waste fat biodiesel,” *Fuel,* vol. 321, p. 123995, 2022.

[13] N.S. Senthur, H. R. Ganesh, S. S. Sulthan and A.M. Avudaiyappan, “Experimental investigation of NO_x emission from eucalyptus-antioxidants blends powered DI diesel engine, ”*Research Journal of Chemistry and Environment.,* vol. 24, pp. 6-9, 2020.

[14] P. Mohamed Shameer and K. Ramesh, “FTIR evaluation on the fuel stability of calophyllum inophyllum biodiesel: Influence of tert-butyl hydroquinone (TBHQ) antioxidant,” *Journal of Mechanical Science and Technology,* vol. 31, no. 7, pp. 3611–3617, 2017.

[15] K. Saibabu, V. Dhana Raju and P. T. Sai, “Experimental studies on the influence of antioxidant additive with waste tamarind biodiesel on the diverse characteristics of diesel engine,” *International Journal of Ambient Energy,* vol. 43, no. 1, pp. 268–277, 2022.

[16] C. Mishra, N. Kumar, P. Mishra, and B. Kar, “In-cylinder combustion and emission characteristics of an agricultural diesel engine fuelled with blends of diesel and oxidatively stabilized Calophyllum Methyl Ester,” *International Mobility Conference,* SAE International, No. 2016-28-0140, 2016.

[17] K. R. Lawrence, Z. Huang, X. P. Nguyen, D. Balasubramanian, V.R. Gangula, R. Doddipalli, S. Bharathy, and A.T. Hoang, “Exploration over combined impacts of modified piston bowl geometry and tert-butyl hydroquinone additive-included biodiesel/diesel blend on diesel engine behaviors,” *Fuel,* vol. 322, p. 124206, 2022.

[18] S. Nogales-Delgado, A. Guiberteau, and J. M. Encinar, “Effect of tert-butylhydroquinone on biodiesel properties during extreme oxidation conditions,” *Fuel,* vol. 310, p. 122339, 2022.

[19] V. EdwinGeo, G. Fol, F. Aloui, S. Thiyagarajan, M. Stanley, A. Sonthalia, K. Brindhadevi, and C. Saravanan, “Experimental analysis to reduce CO2 and other emissions of CRDI CI engine using low viscous biofuels,” *Fuel*, vol. 283, p. 118829, 2021.

[20] Medhat Elkelawy, Hagar Alm-Eldin Bastawissi, Ahmed Abou El-Yazied and S. M. El malla, "Effect of multifunctional fuel additive in diesel/waste oil biodiesel blends on industrial burner flame performance and emission characteristics," *International Journal of Ambient Energy*, vol. 44, no. 1, pp. 1382–1395, 2023.

[21] K. İlçin and Ş. Altun, "Effect of biodiesel addition in a blend of isopropanol-butanol-ethanol and diesel on combustion and emissions of a CRDI engine," *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, vol. 44, no. 2, pp. 4727–4739, 2022.

[22] Katuru Bala Prasad Oliva Meduri and M. E. M. Soudagar, "Effect of split fuel injection strategies on the diverse characteristics of CRDI diesel engine operated with tamarind biodiesel," *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, pp.1-19, 2020.

[23] D. Qi, K. Li, C. Zhang, and T. Wang, "Effect of split injection strategies on diverse characteristics of a common rail direct injection diesel engine operating with diesel-palm oil-ethanol micro-emulsions," *Proceedings of the Institution of Mechanical Engineers, Part A: Journal of Power and Energy*, vol. 236, no. 6, pp. 1210–1226, 2022.

[24] N. Chacko and T. J, "Effect of pilot and post fueling on the combustion and emission characteristics of a light-duty diesel engine powered with diesel and waste cooking biodiesel blend," *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, pp. 1–24, 2020.

[25] C. Joumaa, I. Saad, and G. Younes, "Effect of diesel-biodiesel-ethanol mixtures on corrosion rate of various metals in the presence of tert-butylhydroquinone (TBHQ)," *Quimica Nova*, vol. 47, p. e-20230083, 2024.

[26] P. Saiteja and B. Ashok, "Study on interactive effects of CRDI engine operating parameters through RSM based multi-objective optimization technique for biofuel application," *Energy*, vol. 255, p. 124499, 2022.

[27] S. P. Tamil and G. S. Goteti, "Experimental Analysis of VCR Engine Operated with Prosopis Juliflora Biodiesel Blends," *International Journal of Renewable Energy Research*, vol. 10, no. 2, pp. 978-987, 2020.

[28] H. Sanli, E. Alptekin, and M. Canakci, "Using low viscosity micro-emulsification fuels composed of waste frying oil-diesel fuel-higher bio-alcohols in a turbocharged-CRDI diesel engine," *Fuel*, vol. 308, p. 121966, 2022.

[29] N. Ganesan, K. Viswanathan, S. V Karthic, P. Ekambaram, W. Wu, and Dai.-Viet. N. Vo, "Split injection strategies based RCCI combustion analysis with waste cooking oil biofuel and methanol in an open ECU assisted CRDI engine," *Fuel*, vol. 319, p. 123710, 2022.

[30] E. D. Christensen and R. L. McCormick, "Water Contamination Impacts on Biodiesel Antioxidants and Storage Stability," *Energy and Fuels*, vol. 37, no. 7, pp. 5179–5188, 2023.

[31] A. K. Agarwal, A. Dhar, J. G. Gupta, W. Il Kim, C. S. Lee, and S. Park, "Effect of fuel injection pressure and injection timing on spray characteristics and particulate size–number distribution in a biodiesel fuelled common rail direct injection diesel engine," *Applied Energy*, vol. 130, pp. 212–221, 2014.

[32] D. Babu, V. Thangarasu, and A. Ramanathan, "Artificial neural network approach on forecasting diesel engine characteristics fuelled with waste frying oil biodiesel," *Applied Energy*, vol. 263, p. 114612, 2020.

[33] A. K. Agarwal, A. Dhar, D. K. Srivastava, R. K. Maurya, and A. P. Singh, "Effect of fuel injection pressure on diesel particulate size and number distribution in a CRDI single cylinder research engine," *Fuel*, vol. 107, pp. 84–89, 2013.

[34] P. Tamilselvan and G. Gangeya Srinivasu, "Performance, Emission and Combustion Characteristics of VCR CRDI Diesel Engine Fuelled with n-Butanol Blends," *International Journal of Automotive and Mechanical Engineering*, vol. 16, no. 3, pp. 6825-6843, 2019.

[35] M. Mikulski, K. Duda, and S. Wierzbicki, "Performance and emissions of a CRDI diesel engine fuelled with swine lard methyl esters–diesel mixture," *Fuel*, vol.164, pp.206–219, 2016.

[36] A. Dhar and A. K. Agarwal, "Experimental investigations of the effect of pilot injection on performance, emissions and combustion characteristics of Karanja biodiesel fuelled CRDI engine," *Energy Conversion and Management*, vol. 93, pp. 357–366, 2015.

[37] K. Yamini, P. S. Kishore, and V. Dhana Raju, "Experimental studies on performance, combustion, and emission characteristics of diesel engine powered with subabul seed biodiesel blends," *International Journal of Ambient Energy*, vol. 45, no. 1, p. 2304740, 2024.

[38] S. Manoharan and J. Jeyadharmarajan, "Effect of antioxidant addition on stability and emission aspects of novel biodiesel generated from the yeast Yarrowia lipolytica cultivated on dairy effluent," *Journal of Renewable and Sustainable Energy*, vol. 15, no. 5, p. 053102, 2023.

[39] B. Ashok, K. Nanthagopal, B. Saravanan *et al.*, "A novel study on the effect lemon peel oil as a fuel in CRDI engine at various injection strategies," *Energy Conversion and Management*, vol. 172, pp. 517–528, 2018.

ABBREVIATIONS

20MEOWCO -20 Methyl Esters of Waste Cooking Oil
NOP - Nozzle Opening Pressure
MCRD - Modified Common Rail Diesel
BSFC - Brake Specific Fuel consumption
SFC - Specific Fuel Consumption
CRDI - Common Rail Direct Injection
TDC - Top Dead Centre
BDC - Bottom Dead Centre

CA - Crank Angle
bTDC - Before Top Dead Centre
TBHQ - Tetra-Butyl Hydro Quinone
PY - Pyrogallol
M - Main injection
PI - Pilot Injection
Ppm - Parts Per Million
BHP - Brake Horse Power
BTE - Brake Thermal Efficiency
EGR - Exhaust Gas Reciculation
WCO - Waste Cooking Oil
CPE - Carbon paste electrode
ECU - Elecronic control unit
RTD - Resistance Temperature Detector
B20 - 80% of Petroleum Diesel + 20% of Waste Cooking Oil Bio-Diesel Blend
S20 - 20% sesame biodiesel + 80% diesel fuel.
CTAB - Cetyltrimethylammonium bromide
UBHC - Unburned hydrocarbon
NPPD - N-phenyl-1,4-phenylenediamine
NPAA - 4-Nonyl phenoxy acetic acid
DTBP - di-tert-butyl peroxide
PPDA - P-Phenylenediamine
BHT - Butylated hydroxytoluene
TSME - Tamarind seed methyl ester
PrG - Propyl Gallate
BHA - Butylatedhydroxyanisole
DEA - Di-Ethyl Amine
PHC - Pyridoxine Hydro Chloride
HPLC - high-performance liquid chromatography
SSME - Subabul seed methyl ester