

Article

Pyrolysis Oil Derived from Plastic Bottle Caps: Characterization of Combustion and Emissions in a Diesel Engine

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Abstract: Recycling used plastic can help reduce the amount of plastic waste generated. Existing methods, namely the process of pyrolysis, are chemical heating processes that decompose plastics in the absence of oxygen. This decomposes the plastics in a controlled environment in order to produce fuel from waste. The present study consequently investigated the physical and chemical properties of pyrolysis oil derived from plastic bottle caps (WPBCO) and the effects on the engine performance and emission characteristics of a diesel engine operating on WPBCO. The experiments were conducted with a single-cylinder diesel engine operating at a constant 1500 rpm under various engine loading conditions. The experimental results of the chemical properties of test fuels indicated that WPBCO and diesel fuels have similar functional groups and chemical components. In comparison, WPBCO has a lower kinematic viscosity, density, specific gravity, flash point, fire point, cetane index, and distillation behavior than diesel fuel. However, WPBCO has a high gross calorific value, which makes it a suitable replacement for fossil fuel. In comparison to diesel fuel, the use of WPBCO in diesel engines results in increased brake-specific fuel consumption (BSFC) and brake thermal efficiency (BTE) under all load conditions. The combustion characteristics of the engine indicate that the use of WPBCO resulted in decreased in-cylinder pressure (ICP), rate of heat release (RoHR), and combustion stability compared to diesel fuel. In addition, the combustion of WPBCO advances the start of combustion more strongly than diesel fuel. The use of WPBCO increased emissions of NO_x, CO, HC, and smoke. In addition, the particulate matter (PM) analysis showed that the combustion of WPBCO generated a higher PM concentration than diesel fuel. When WPBCO was combusted, the maximum rate of soot oxidation required a lower temperature, meaning that oxidizing the soot took less energy and that it was easier to break down the soot.

Keywords: pyrolysis oil; plastic bottle cap; diesel engine; combustion characteristics; emissions



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1. Introduction

The depletion of fossil fuels, fluctuations in fuel prices, global warming concerns, and more stringent emissions legislation are factors that have led to an increase in the amount of research being undertaken to improve engine characteristics (e.g., developing advanced combustion technology and innovative fuel injection strategies for low carbon emissions [1,2]) and cleaner sustainable fuels (e.g., biodiesels [3] and alcohols [4]). It has been proven that the carbon monoxide and particulate matter emissions can be improved by using biodiesels and alcohols as pure or blended components in internal combustion engines. Due to the limitations of domestic petroleum oil production and high oil demands, the government developed the Thailand integrated energy blueprint

(2015–2036) to decrease net energy imports. The reduction and replacement of fossil fuels with biofuels such as ethanol, biodiesel, and pyrolysis oil are included in this plan. With increasing and considerable quantities of municipal solid waste being generated, the conversion of plastic waste into liquid fuel has received increasing attention from researchers.

Plastic is an important material in the everyday lives of individuals because it is lightweight, strong, flexible, and durable, has a low production cost, and can be produced to meet a variety of requirements, including the current situation regarding the COVID-19 pandemic. People's behaviors have changed as they use more and more online ordering services, which has resulted in an ever-increasing amount of plastic waste [5,6]. According to a recent report, global plastic use is 335 billion tons per year, with an estimated increase in plastic usage of more than 12 billion tons by 2050. The utilization of plastics has increased, which is one of the main causes of environmental problems, especially in countries with insufficient waste management systems. This is due to the fact that many plastics take a long time to decompose and that specific plastics are not biodegradable. Plastics can also break down into microplastics, which harm the environment [7].

Thailand is country that produces the sixth-largest amount of plastic waste globally, followed by China, Indonesia, Philippines, Vietnam, and Sri Lanka. As a result, Thailand is facing environmental problems caused by increasing amounts of plastic waste [8]. Regarding the municipal solid waste (MSW) situation in Thailand, in 2021 it was found that the total amount of solid waste reached 24.98 million; of this amount, 3.89 million, or 16%, was recyclable waste [9]. The report pointed out that some of the solid waste was incorrectly disposed of or leaked into the environment. Furthermore, MSW includes a significant amount of plastic waste, with single-use plastic containers found in all of the major plastic waste categories. Containers, such as those used for soft drinks, milk, and water, have the greatest tonnage. More plastic waste is generated by single-use plastic packaging. There are many approaches to solving the problem of plastic waste, such as reducing use, reusing, and recycling, or the use of synthetic plastic waste that can be burned in a controlled standard incinerator. However, compared to the total amount of plastic waste made, a very small amount is compensated for in these manners. At present, the conversion of plastic waste to energy as fuel through the pyrolysis process is one approach that can help to solve environmental problems and can also help to reduce the use of conventional fossil fuels. Furthermore, avoiding these problems by making fuel out of high-density polyethylene (HDPE) plastic bottle caps is a way to transfer benefits and value.

A previous study indicates that the end products of the process of pyrolyzing plastic waste consist of liquid oil, gases, and solid products (char). The production yield is dependent on the type and composition of the plastic waste. Unlike pyrolysis oil, the approaches to treating and deriving benefits from the solid residues obtained from the pyrolysis process are undergoing research and development. It was reported that char could be used as a heat source due to its high heat capacity with respect to hot carrier gas [10]. Char from the biomass pyrolysis was reportedly used as an adsorbent to remove mercury in a flue gas coal-fired power plant [11]. The liquid oil obtained from the pyrolysis process generally consists of impurities such as sulfur and nitrogen compounds and polycyclic aromatic hydrocarbons (PAHs), which are considered a drawback of pyrolysis oil [12]. To reduce the formation of sulfur compounds, calcium carbonate and natural zeolite have been used to adsorb sulfur dioxide from pyrolysis oils. As the higher reaction temperatures during the pyrolysis process tend to accelerate the formation of sulfur and nitrogen compounds, a low reaction temperature is recommended for the pyrolysis process [13]. In addition, it was reported that higher reaction temperatures and heating rates also favor the formation of PAHs, so the optimum temperature and heating rate are necessary to limit the amounts of such impurities that are present in the pyrolysis oil. Volatile products having a shorter residence time in the reactor during the pyrolysis process was revealed to be a promising approach to controlling the formation of PAHs [14]. Small micron particle contamination present in the oil can directly affect the engine performance and engine life. The fuel injector

may become clogged and less fuel may be used in the combustion process, resulting in undesirable emissions and poor engine performance. In addition, the presence of small solid particles in the oil may create engine wear and shorten the engine's life. It was reported that 2–3 μm particles constitute the most critical size of particle present in the oil film used to lubricate the engine moving parts (e.g., the piston ring) in order to avoid engine damage [15]. A previous investigation also reported that, when the lubrication oil was filtered down to 7 μm , engine wear was minimized and the relative engine life was more than five times longer [16].

The properties of the pyrolysis oil obtained from plastic waste are comparable to those of petroleum fuel, suggesting that pyrolysis oil derived from plastic waste may be a better alternative owing to its comparable calorific value to diesel. Moreover, it can also be used as an alternative fuel in compression ignition engines [17]. In contrast, the experimental results of several published studies show that the usage of pyrolysis oil in diesel engines resulted in an increase in brake-specific fuel consumption (BSFC) and brake thermal efficiency (BTE) in comparison to diesel fuel. Nitrogen oxides (NOX), unburned hydrocarbons (HC), carbon monoxide (CO), and smoke emissions tend to increase with the usage of pyrolysis oil due to its combustion [18]. Moreover, pyrolysis oil has a significant effect on an engine's combustion characteristics, such that the use of pyrolysis oil increases the ignition delay period, the rate of heat release, and the in-cylinder pressure, which are all essential parameters for CI engine combustion characteristics [19–21]. Nevertheless, some researchers have observed that the engine performance of pyrolysis oil is higher than that of diesel fuel, and that decrease in NOX, CO, and smoke emissions are seen when pyrolysis oil is utilized as fuel in CI engines [22,23]. The goal of this study is to determine whether it would be possible to use pyrolysis oil made from plastic bottle caps as an alternative fuel, in order that the effects of this fuel on emissions and on the combustion characteristics of the engine can be studied.

2. Materials and Methods

2.1. Conversion of Waste Plastic Bottle Caps into Pyrolysis Oil

High-density polyethylene (HDPE) waste bottle caps are converted into useful fuel through the pyrolysis process, which is a process of thermal decomposition that operates in the absence of oxygen. In Muang District, Nakhon Ratchasima, Thailand, we collected waste plastic bottle caps from municipal solid waste and cut them into round 1 cm^2 pieces for raw materials. The raw materials were then placed into the reactor chamber. Regarding the process conditions, a laboratory-scale fixed-bed reactor was used for pyrolysis at 450 $^{\circ}\text{C}$ under atmospheric pressure with a constant heating rate of 15 $^{\circ}\text{C}/\text{min}$ and a reaction time of 30 min. Experiments were carried out at the Agricultural Engineering Laboratory, Suranaree University of Technology.

2.2. Chemical Characteristics of Test Fuels

The analysis of chemical compounds in the test fuels was performed using gas chromatography-mass spectrometry (GC-MS), which, for both quantitative and qualitative analysis, is one of the most popular analytical techniques for the determination of chemical compounds in solid, liquid, and gas mixtures. Based on the different solubility and adsorption capacities of each substance in the mobile phase and the stationary phase, the gas chromatographic components consist of a carrier gas, an injector port, a column and a column oven, a detector, and a computer with software for processing. In this experimental investigation, data were analyzed using gas chromatography (Agilent Technologies 7890A) connected to a mass selective detector (Agilent Technologies 7693 ALS). The analytical conditions of the GC-MS were the same as those detailed in [24] and are listed in Table 1.

Table 1. The analytical conditions of the GC–MS.

Gas Chromatography Condition	
Column oven temperature	50 °C
Injection mode	Split
Split ratio	20:1
Injection volume	1 µL
Injection temperature	350 °C
Diameter and length column	0.25 mm/60 m
Column flow	1.0 mL/min
Carrier gas	Helium
Mass spectrometry condition	
Scan type	MS1 scan
Source temperature	250 °C
Mass to charge range	35–550 <i>m/z</i>

Fourier transform infrared spectroscopy (FT–IR) is a technique used to determine the functional groups of organic matter; it can analyze solid, liquid, and gaseous materials based on the absorption of infrared radiation in a specific wavelength range, regardless of the structure of the rest of the molecules. The test fuels for this study were taken using Bruker (TENSOR27–Hyperion) and were scanned in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1} . The signal reading is displayed as a graph plotted against the light that passes through the test sample by calculating the percentage of transmission. The ratio between the intensity of the light passing through the test sample and the incident light intensity of the test sample multiplied by 100 is shown on the Y-axis, and the wave number is shown on the X-axis. In addition, the ultimate analysis is an important analysis technique that can be used to investigate the elemental composition of test fuels, in which a CHNS elemental analyzer (LECO CHN628/628S) is used for the elemental analysis of diesel fuel and WPBCO. The chemical characteristics of the test fuels were tested at the Center for Scientific and Technology Equipment, Suranaree University of Technology, Thailand.

2.3. Physicochemical Characteristics of Test Fuels

The physicochemical characteristics of diesel fuel and WPBCO in terms of their properties such as kinematic viscosity, specific gravity, density, flash point, fire point, gross calorific value, cetane index, and distillation temperature were analyzed under the American Society for Testing and Materials (ASTM) standard test method. Their physicochemical characteristics are compared with those of commercial-grade diesel fuel. The commercial-grade diesel fuel that is used as a baseline fuel is widely available at public fuel stations; these blends contain 7% biodiesel and mainly use crude palm oil as a feedstock. For the experimental testing of physicochemical characteristics, the kinematic viscosity was measured using a Cannon–Fenske capillary viscometer tube at the required test temperature of 40 °C with the ASTM D445 method. The specific gravity was determined by the hydrometer at the required test temperature of 15 °C, along with the calculation of the density according to the ASTM D1298 method. The flash point and fire point of the test fuels were assessed with a Pensky–Martin closed cup tester based on the ASTM D93 method. The energy contents of test fuels were determined by a bomb calorimeter (AC–600 Calorimeter, LECO, St. Joseph, MI, USA) in the form of gross calorific value (high heating value) following the standard ASTM D240 methods. Additionally, the distillation temperature was found by following the steps in the ASTM D86 methods, and the cetane index was found by using the density and the distillation temperatures of 10, 50, and 90% recovery according to the ASTM D4737 method [25].

2.4. Experimental Setup and Procedure for Particulate Matter (PM) Analysis

To test and compare the experimental results of WPBCO with diesel fuel, a Kirloskar TV1 diesel engine (1 cylinder, 661 cc, rated output of 3.5 kW at 1500 rpm) was used. The

test engine was operated at a constant 1500 rpm with 4 different engine operating loads (25%, 50%, 75%, and 100%) of maximum engine torque for both fuels. Using a water-cooled eddy current dynamometer, the engine performance, combustion characteristics, and exhaust gas emissions were evaluated under different loads. Figure 1 represents the experimental set-up. Diesel fuel was used as a baseline for comparison with WPBCO during engine run testing. The air flow rate to the engine was evaluated using an air box, and fuel consumption was measured volumetrically using a burette and a digital timer. A Kubler crank angle sensor with a crank angle degree with precision of 0.1 detected the engine crank angle position. The in-cylinder pressure was measured using a PCB piezotronic pressure transducer connected to a charge amplifier. At each crank angle, the in-cylinder pressure data were averaged for 100 cycles. EngineSoft was used to analyze the combustion characteristics of the engine under various engine loads. In case the calculation of heat balance is considered, the relevant parameters consisted of jacket cooling water flow (F1), calorimeter water flow (F2), jacket water inlet temperature (T1), jacket water outlet temperature (T2), calorimeter water inlet temperature (T3), calorimeter water outlet temperature (T4), exhaust gas to calorimeter inlet temperature (T5) and exhaust gas from calorimeter outlet temperature (T6) are recorded. Using an emission analyzer (Testo 350 flue gas analyzer), the exhaust gas emissions were measured (NOX, CO, and HC). Meanwhile, the smoke index was measured using a smoke meter (Testo 308 smoke meter). The technical specifications of the gas-analyzing equipment [26] and other measuring instruments [27] are shown in Table 2. After the engine had attained a steady state under each condition, data were acquired by observing the engine load and engine speed. For each refueling, the engine was operated for 10 min to consume the fuel that had been entrapped in the fuel lines. The repeatability of the readings was ensured by repeating them three times, and the average values of parameters related to the evaluation of engine performance and exhaust emissions were reported. Additionally, the 95% confidence interval was considered to establish the statistical significance of the result trends.

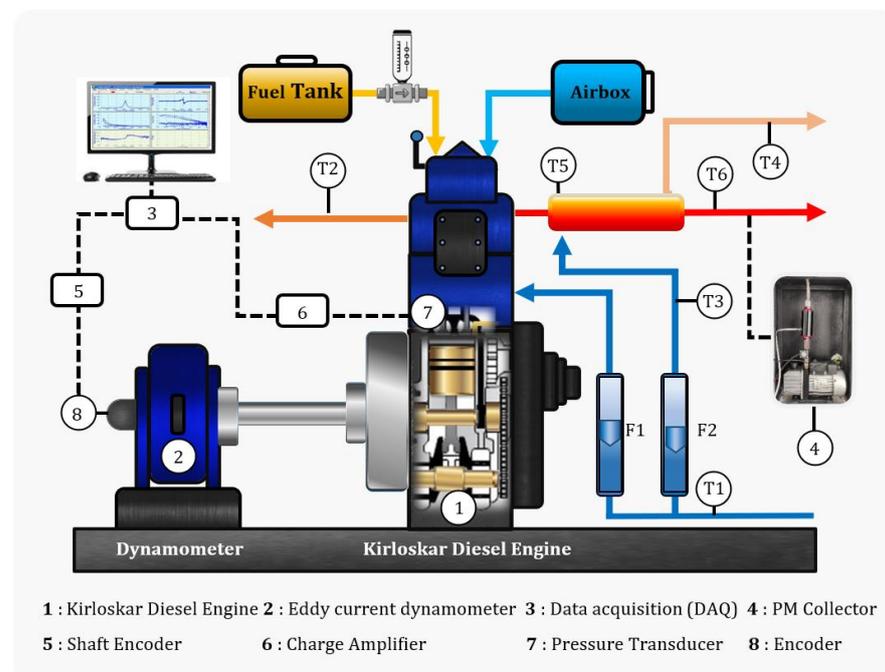


Figure 1. Layout of the diesel engine test rig.

Table 2. Technical specification of measuring instruments.

Parameters	Measuring Technique	Accuracy
NO	Chemiluminescence	±5% of reading
NO ₂	Chemiluminescence	±5% of reading
CO	Nondispersive infrared	±5% of reading
HC	Flame ionization detector	±10% of reading
Smoke	Photodiode (filter paper)	±0.2 smoke index
Engine load	Strain gauge type load cell	±10 N
Engine speed	Magnetic pickup principle	±10 rpm
Fuel flow rate	Volumetric measurement	±0.1 cc
Time	Stop watch	±0.1 s
Temperature	Thermocouple	±1 °C
In-cylinder pressure	Piezoelectric sensor	±0.1 kg
Crank angle encoder	Optical sensor	±1 deg

The analysis of particulate matter (PM) in the exhaust gas of a diesel engine using pyrolysis oil derived from plastic bottle caps was investigated by thermogravimetric analysis (TGA) in order to determine the thermal decomposition behaviors of WPBCO and diesel fuel, producing a derivative thermogravimetric analysis (DTG) curve. The results of the TGA can be used to determine oxidation kinetics parameters, which are crucial characteristics for evaluating oxidation activity [28]. The PM characteristics generated during the combustion of the test fuels were investigated under the same conditions. Then, using a PM collector that was installed on the tail exhaust pipe of a diesel engine and keeping the exhaust gas flow rate in the PM collector at around 15 L/min, PM was measured in order to determine the PM concentration. The engine was operated at a constant speed of 1500 rpm with a maximum engine torque of 50% during the 30 min that it took to load PM onto the filter paper. The PM concentration from the combustion of test fuels was collected using grade GF/C Whatman glass microfiber filter paper that was 47 mm in diameter with a pore size of 1.2 microns. Using an analytical balance (Sartorius BP221S), the weight of the PM emissions loaded on the filter paper was calculated by weighing the filter paper before and after PM collection in order to assess the weight of the PM. Thermogravimetric (TGA) analysis (Mettler Toledo, Columbus, OH, USA) was used to characterize soot as a component of PM. In all TGA experiments, the weight of the PM collected on the loaded TGA filter was around 2.0 to 5.0 mg; this matter was then placed in the sample basket of the thermogravimetric analyzer for heating in the TGA according to the following program. Setting the initial oxygen atmosphere at a constant flow rate of 60.0 mL/min was the first step in the heating program. In the second step, the filter was heated from 35 to 110 °C at a rate of 5.00 °C/min in an oxygen atmosphere. The temperature was held at 110 °C for 5 min. Under the oxygen atmosphere, the PM-loaded filter was reheated from 110 °C to 700 °C at a heating rate of 5.00 °C/min. Finally, the temperature was held at 700 °C for 5 min.

3. Results and Discussion

3.1. Chemical Characteristics of Test Fuels

Figure 2 represents the GC–MS chromatograms of diesel fuel and WPBCO obtained by comparing the National Institute of Standards and Technology (NIST) library, which is based on the percentage of peak results calculated from the total ion current (TIC) area. The peaks in the spectra correspond to various hydrocarbons. The area percent of the peak for a compound is correlated with the percentage of that compound in the test fuels. Additionally, Table 3 shows the chemicals that are found in diesel fuel, and Table 4 shows the chemicals that are present in WPBCO. Because both fuels consist of hundreds of different molecule types, their chemical composition is very complicated. The GC–MS results of the components present in different hydrocarbons in WPBCO are mostly the alkanes and alkenes with carbon numbers of C7–C28, and similar findings were also reported in the results [29]. Meanwhile, diesel fuel has carbon numbers ranging from C8–C29. According to the results,

the average molecular weight of WPBCO was 240.61 g/mol, which is more than diesel fuel at 229.99 g/mol. Diesel fuel is made up of hydrocarbons, mostly paraffin (69.43%), which is the main compound found in petroleum fuel, followed by methyl ester compounds (20.15%), olefins (2.39%), and aromatics (4.88%). Methyl ester compounds were detected in diesel fuel. This is because the diesel fuel used for the analysis is commercial diesel fuel with a biodiesel blend ratio of 7 percent by volume. The methyl ester compounds are oxygen-containing compounds; this is one of the factors that helps the combustion process of an engine to go smoothly and decreases the amount of emissions that it emits. WPBCO contains paraffin (49.91%), followed by olefins (46.96%), and others (3.13%). The carbon number ranges from C6–C12, C13–C18, and C19–C23, and more than C23 can be used to characterize the GC–MS results as shown in Figure 3. According to the GC–MS results, about 43.77% of WPBCO is comprised of molecules in the C13–C18 range, which is close to the range of diesel fuel. This suggests that it has a high concentration of diesel fuel components.

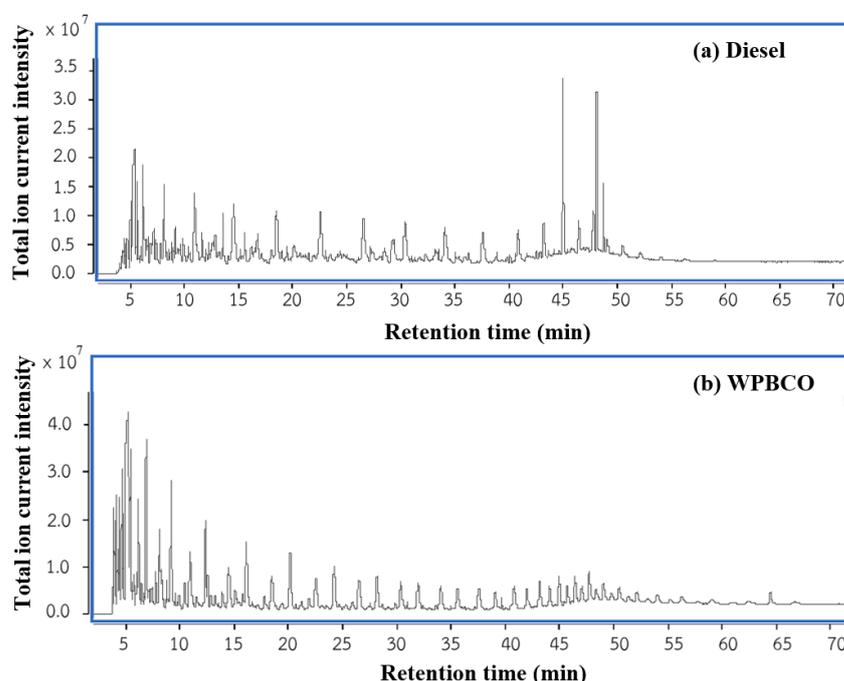


Figure 2. GC–MS chromatograms for (a) diesel fuel and (b) WPBCO.

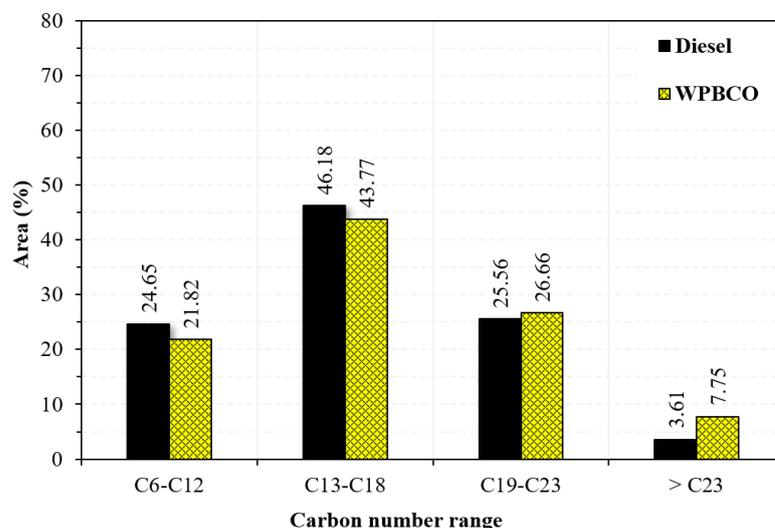


Figure 3. Carbon number range for diesel fuel and WPBCO by GC–MS analysis.

Table 3. The identification and distribution of the compounds for diesel fuel.

RT (min)	Compound Name	Chemical Information		
		Formula	MW	Area (%)
4.35	Octane	C ₈ H ₁₈	114.14	0.78
4.49	Cyclohexane, 1,4-dimethyl-	C ₈ H ₁₆	112.13	0.82
5.05	Nonane	C ₉ H ₂₀	128.16	1.67
5.58	Nonane, 4-methyl-	C ₁₀ H ₂₂	142.17	1.61
6.16	Decane	C ₁₀ H ₂₂	142.17	3.62
8.10	Undecane	C ₁₁ H ₂₄	156.19	4.18
9.13	p-Xylene	C ₈ H ₁₀	106.08	0.94
9.88	trans-2-Dodecen-1-ol	C ₁₂ H ₂₄ O	184.18	1.09
10.93	Dodecane	C ₁₂ H ₂₆	170.20	5.99
11.62	Benzene, 1-ethyl-3-methyl-	C ₉ H ₁₂	120.09	0.92
13.55	Benzene, 1,2,3-trimethyl-	C ₉ H ₁₂	120.09	1.62
14.50	Tridecane	C ₁₃ H ₂₈	184.22	6.39
15.56	Benzene, 1,2,4-trimethyl-	C ₉ H ₁₂	120.09	1.40
18.49	Tetradecane	C ₁₄ H ₃₀	198.23	6.52
20.11	1-Tetradecene	C ₁₄ H ₂₈	196.22	1.57
22.55	Pentadecane	C ₁₅ H ₃₂	212.25	5.66
26.53	Hexadecane	C ₁₆ H ₃₄	226.27	5.95
30.37	Heptadecane	C ₁₇ H ₃₆	240.28	5.69
34.05	Octadecane	C ₁₈ H ₃₈	254.30	4.30
37.55	Nonadecane	C ₁₉ H ₄₀	268.31	4.01
40.80	Eicosane	C ₂₀ H ₄₂	282.33	3.90
43.18	Heneicosane	C ₂₁ H ₄₄	296.34	3.19
44.96	Hexadecanoic acid, methyl ester	C ₁₇ H ₃₄ O ₂	270.26	10.11
46.43	Tricosane	C ₂₃ H ₄₈	324.38	2.36
47.79	Methyl stearate	C ₁₉ H ₃₈ O ₂	298.29	2.06
48.07	11-Octadecenoic acid, methyl ester	C ₁₉ H ₃₆ O ₂	296.27	7.59
48.68	Linoleic acid, methyl ester	C ₁₉ H ₃₄ O ₂	294.26	2.45
49.03	Pentacosane	C ₂₅ H ₅₂	352.41	1.19
50.44	Hexacosane	C ₂₆ H ₅₄	366.42	1.13
52.10	Heptacosane	C ₂₇ H ₅₆	380.44	0.62
53.97	Octacosane	C ₂₈ H ₅₈	394.45	0.34
56.22	Nonacosane	C ₂₉ H ₆₀	408.47	0.33

The analysis of the functional groups of test fuels using FT-IR spectroscopy is a widely accepted approach for identifying the compound chemical functional groups that are present in the fuel. This study compares the results of diesel fuel analysis. The spectrum analysis results are shown in Figure 4. It can be seen that the peak FT-IR for diesel fuel occurs at different wave numbers, including 2954 cm⁻¹, 2922 cm⁻¹, 2853 cm⁻¹, 1746 cm⁻¹, 1605 cm⁻¹, 1460 cm⁻¹, 1377 cm⁻¹, 1169 cm⁻¹, 806 cm⁻¹, 766 cm⁻¹, 722 cm⁻¹, 539 cm⁻¹, 437 cm⁻¹, and 409 cm⁻¹, which correspond to the locations of the bonds of C-H stretching, C-H bending, C=C stretching, CH bending, C=C bending, and C-Br stretching; meanwhile, the wave numbers 1746 cm⁻¹ and 1169 cm⁻¹ indicate the locations of the ester functional groups (C=O and CO), and are consistent with the results of the aforementioned GC-MS analysis before methyl ester compounds were detected. The functional groups of WPBCO were taken into account, and more than 20 FT-IR peaks show that these functional groups had functional groups close to diesel fuel. The functional groups C-H stretching (alkenes) and C-O stretching (aromatic esters) were found in the WPBCO, but not in diesel fuel, as shown in Table 5 for wave numbers between 3100 and 3000 cm⁻¹ and between 1310 and 1250 cm⁻¹.

Table 4. The identification and distribution of the compounds for WPBCO.

RT (min)	Compound Name	Chemical Information		
		Formula	MW	Area (%)
4.15	Heptane	C ₇ H ₁₆	100.13	0.70
4.49	Octane	C ₈ H ₁₈	114.14	1.31
4.73	2-Octene	C ₈ H ₁₆	112.13	0.89
6.18	Decane	C ₁₀ H ₂₂	142.17	3.42
6.88	1-Decene	C ₁₀ H ₂₀	140.16	2.73
8.02	Undecane	C ₁₁ H ₂₄	156.19	3.21
9.08	1-Undecene	C ₁₁ H ₂₂	154.17	3.27
10.73	Dodecane	C ₁₂ H ₂₆	170.20	3.59
12.12	1-Dodecene	C ₁₂ H ₂₄	168.19	2.71
14.16	Tridecane	C ₁₃ H ₂₈	184.22	4.66
15.78	1-Tridecene	C ₁₃ H ₂₆	182.20	2.55
18.01	Tetradecane	C ₁₄ H ₃₀	198.23	4.32
19.73	1-Tetradecene	C ₁₄ H ₂₈	196.22	2.58
22.00	Pentadecane	C ₁₅ H ₃₂	212.25	4.82
23.74	1-Pentadecene	C ₁₅ H ₃₀	210.23	2.76
25.95	Hexadecane	C ₁₆ H ₃₄	226.27	5.41
27.68	1-Hexadecene	C ₁₆ H ₃₂	224.25	2.53
29.79	Heptadecane	C ₁₇ H ₃₆	240.28	4.79
31.48	1-Heptadecene	C ₁₇ H ₃₄	238.27	2.60
33.49	Octadecane	C ₁₈ H ₃₈	254.30	5.06
35.13	1-Octadecene	C ₁₈ H ₃₆	252.28	1.69
37.01	Nonadecane	C ₁₉ H ₄₀	268.31	4.45
38.63	1-Nonadecene	C ₁₉ H ₃₈	266.30	1.58
40.36	Eicosane	C ₂₀ H ₄₂	282.33	4.52
41.67	1-Eicosene	C ₂₀ H ₄₀	280.31	1.31
42.84	Heneicosane	C ₂₁ H ₄₄	296.34	4.27
43.82	10-Heneicosene (c,t)	C ₂₁ H ₄₂	294.33	1.33
44.70	Docosane	C ₂₂ H ₄₆	310.36	3.66
45.51	1-Docosene	C ₂₂ H ₄₄	308.34	1.67
46.22	Tricosane	C ₂₃ H ₄₈	324.38	2.95
46.91	1-Tricosene	C ₂₃ H ₄₆	322.36	0.89
47.54	Tetracosane	C ₂₄ H ₅₀	338.39	2.40
48.88	Pentacosane	C ₂₅ H ₅₂	352.41	1.83
50.31	Hexacosane	C ₂₆ H ₅₄	366.42	1.54
51.93	Heptacosane	C ₂₇ H ₅₆	380.44	1.12
53.83	Octacosane	C ₂₈ H ₅₈	394.45	0.87

Table 5. The functional group composition present in diesel fuel and WPBCO.

Wavelength (cm ⁻¹)	Type of Vibration (Functional Group)	Diesel	WPBCO
3100–3000	C–H stretching (Alkenes)	–	✓
3000–2840	C–H stretching (Alkanes)	✓	✓
2830–2695	C–H stretching (Aldehydes)	–	–
2000–1650	C–H bending (Aromatic compounds)	✓	✓
1750–1735	C=O stretching (Esters)	✓	–
1670–1600	C=C stretching (Alkenes)	✓	✓
1465–1380	C–H bending (Alkanes)	✓	✓
1310–1250	C–O stretching (Aromatic esters)	–	✓
1210–1163	C–O stretching (Esters)	✓	–
1000–665	C=C bending (Alkenes)	✓	✓
690–515	C–Br stretching (Halo compounds)	✓	✓

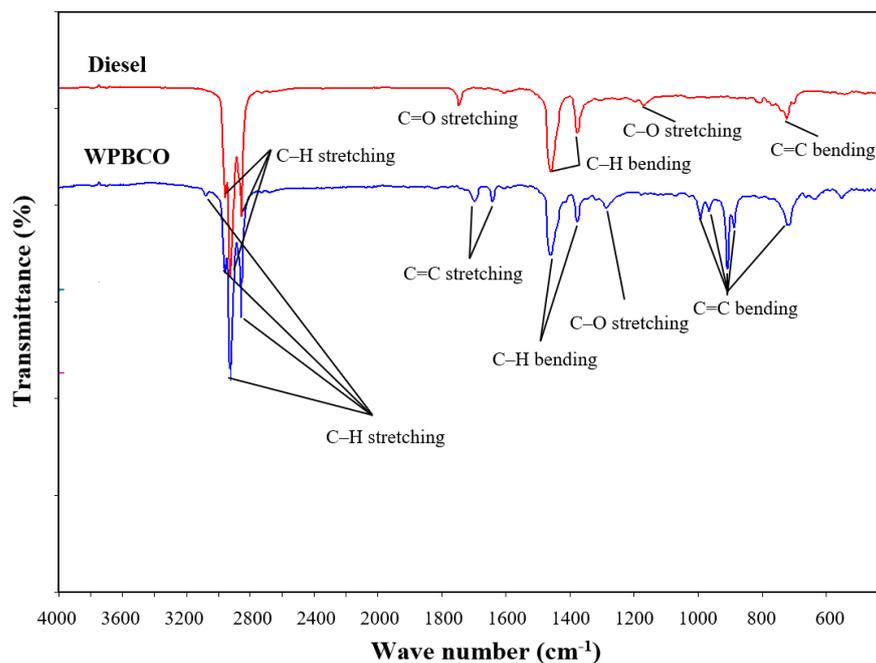


Figure 4. FT-IR spectrum analysis results for diesel fuel and WPBCO.

The percentages of carbon (C), hydrogen (H), nitrogen (N), and sulphur (S) present in diesel fuel and WPBCO were measured by CHNS analysis, and the results of the elemental analysis for both fuels are presented in Table 6. The results show that WPBCO contains carbon (C) and hydrogen (H) as the main constituents that indicate its fuel efficiency. The amounts of carbon and hydrogen for WPBCO are approximately 66.899 wt% and 11.906 wt%, respectively. When comparing carbon and hydrogen to diesel, WPBCO has less carbon than diesel fuel and about the same amount of hydrogen, which means it has a lower energy content (heating value) [30]. Moreover, the sulphur (S) contained in WPBCO (which, after combustion in the engine, forms sulfates and binds to other exhaust gas emissions) produces particulate matter. It also produces sulfur oxides when reacted with nitrogen oxides and combines with atmospheric water vapor to produce acid rain, which has a negative impact on the environment. Essentially, fossil fuel combustion is the process of burning a fuel that is primarily composed of hydrocarbons reacting with oxygen in the air. The amount of energy released during the combustion of fuel depends on the oxidation of carbon in the fuel in relation to the H/C ratio. When the fuel has a higher H/C ratio, it results in a lower oxidation stage and more energy is released during the oxidation reaction [31].

Table 6. CHNS elemental analysis of diesel fuel and WPBCO.

Elements	CHNS Elemental Composition (wt%)	
	Diesel	WPBCO
Carbon (C)	83.230	66.899
Hydrogen (H)	11.020	11.906
Nitrogen (N)	0.018	Not detected
Sulfur (S)	0.000	0.699

3.2. Physicochemical Characteristics of Test Fuels

The physicochemical properties of diesel fuel and WPBCO are the kinematic viscosity, specific gravity, density, flash point, fire point, gross calorific value, cetane index, and distillation temperature. These are the most important physical and chemical properties of fuel for use in diesel engines, and their parameters affect the engine performance and

combustion characteristics. The physicochemical properties of diesel fuel and WPBCO were analyzed according to the standard test method, which was determined by the national regulation of the Department of Energy Business, Ministry of Energy, Thailand [32]. The results of the fuel properties of both fuels are summarized in Table 7. It can be seen that the kinematic viscosity of WPBCO was lower than that of diesel fuel and than the limits of the diesel fuel range. However, its low kinematic viscosity value can provide improved atomization and lead to better combustion characteristics [33]. The specific gravity, density, flash point, fire point, and cetane index of WPBCO were lower than those of diesel fuel. Regarding the energy content of WPBCO, it can be observed that WPBCO has an 8.74% lower gross calorific value than diesel fuel. This reason for this is related to the chemical characteristics of WPBCO, as the low carbon composition leads to reductions in the flash point, fire point, cetane index, distillation temperature, and gross calorific value [34]. Table 7 additionally shows the WPBCO distillation temperature results. The distillation temperature range obtained for WPBCO is in the range of 78–316 °C. Due to WPBCO, the presence of carbon numbers varies in gasoline and diesel fuel. Its composition has been shown to be lower than that of diesel fuel. Based on experiments and a study of the properties of the fuel, WPBCO can be potentially used as an alternative fuel. The authors studied the effects of WPBCO on engine performance, combustion, and exhaust gas emissions and compared them to diesel fuel operations.

Table 7. Physicochemical properties of diesel fuel and WPBCO.

Physicochemical Properties	Test Method	Limits	Diesel	WPBCO
Kinematic viscosity at 40 °C (cSt)	ASTM D445	1.8–4.1	3.37	1.30
Specific gravity at 15 °C	ASTM D1298	0.81–0.87	0.830	0.770
Density @ 15 °C (kg/m ³)	ASTM D1298	–	829	769
Flash point (°C)	ASTM D93	>52	78	32
Fire point (°C)	ASTM D93	–	86	36
Gross calorific value (MJ/kg)	ASTM D240	–	43.48	39.68
Cetane index	ASTM D4737	>50	61.09	51.78
Distillation temperature (°C)	ASTM D86			
IBP (°C)	ASTM D86	–	188	78
10% Recovered (°C)	ASTM D86	–	228	144
50% Recovered (°C)	ASTM D86	–	290	198
90% Recovered (°C)	ASTM D86	<357	342	294
FBP (°C)	ASTM D86	–	348	316

3.3. Analysis of Engine Performance

In this section, the engine performance of the test engine for pyrolysis oil derived from waste plastic bottle caps was examined and compared to diesel fuel operations in terms of brake-specific fuel consumption (BSFC) and brake thermal efficiency (BTE). These variables are directly measurable and calculable from the engine test. The engine performance experimental results can be analyzed as follows:

Brake-specific fuel consumption (BSFC) is an important parameter for engine performance analysis. It is a fundamental parameter used to assess the fuel consumption of an engine at various operating conditions (low BSFC indicates fuel economy) by showing the relationship of fuel mass flow rate per unit of brake power output produced by the engine [35]. The units commonly used to express BSFC are grams per kilowatt-hour (g/kW-h). The design of the fuel injection system and fuel properties such as calorific value, density, and viscosity are significant factors affecting BSFC [36]. Figure 5 shows the variation in BSFC with respect to engine load for diesel fuel and WPBCO. It can be observed that the BSFC decreases as the engine load increases for both fuels. This is the result of the engine using more fuel at higher loads under the same experimental conditions. Other reasons for the decrease in the BSFC include a decrease in the residence time of the combustion gases and an increase in volumetric efficiency [22]. The WPBCO presents a BSFC higher than diesel fuel by 9.64% at high engine loads. Due to the lower energy

content of WPBCO when compared to diesel fuel, its higher fuel consumption causes its higher fuel consumption to produce the same power output [37,38].

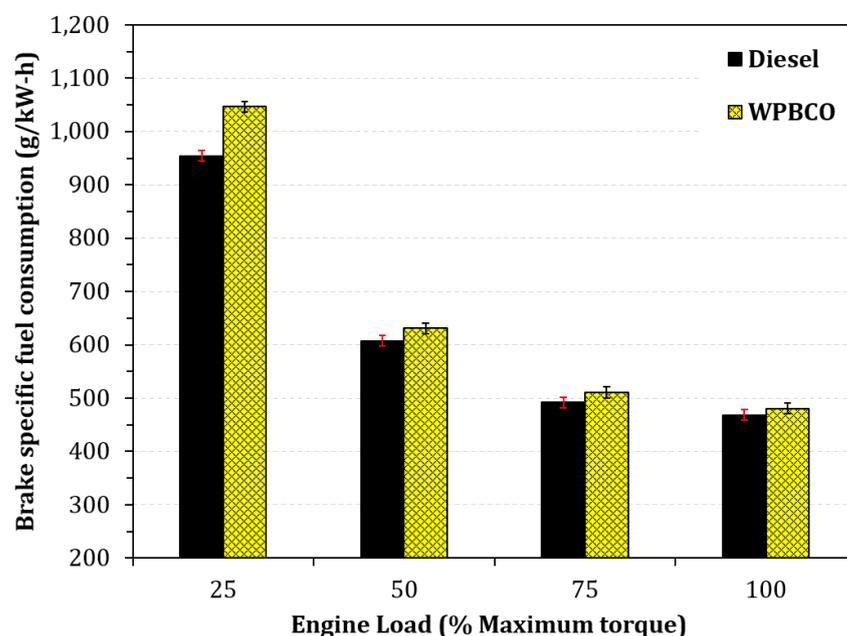


Figure 5. Variation in brake-specific fuel consumption with respect to the engine load.

Brake thermal efficiency (BTE) is a parameter used to describe the ability to convert the thermal energy obtained from a fuel into mechanical energy for an internal combustion engine. The thermal efficiency depends on the engine design, fuel properties, and engine operating conditions, etc. [39]. Figure 6 shows the variation in BTE with respect to engine load for diesel fuel and WPBCO. As for the experimental results, it can be noted that the BTE increases as the engine load increases for both fuels. This is due to the increases in temperature and pressure within the combustion chamber as the increase in the engine load results in higher conversion and less heat loss, which can be attributed to the combustion improvement [40]. When comparing diesel fuel and WPBCO, the WPBCO has a significantly higher BTE compared to diesel fuel for all engine load operations. Moreover, the BTE of WPBCO is 6.85% higher than diesel fuel at high engine loads. The use of WPBCO improves combustion efficiency due to the presence of oxygenated compounds in the composition of pyrolysis oil [22,41]. Lower viscosity and density promote a complete combustion of the air–fuel mixture [42–44]. The reason for this is the increase in BTE for WPBCO compared to diesel fuel.

3.4. Analysis of Combustion Characteristics

In this section, the combustion characteristics of WPBCO compared to diesel fuel in terms of in-cylinder pressure (ICP), the rate of heat release (RoHR), and the coefficient of variance of maximum in-cylinder pressure (COVPmax) were investigated. These are important parameters that are used to analyze the stability of fuel combustion in the combustion chamber of the diesel engine. The experimental results of combustion characteristics can be analyzed as follows:

The ICP is the most important parameter for understanding how an engine works, since it provides useful information on combustion in the combustion chamber [45]. The cylinder pressure of the engine can be measured by a pressure transducer mounted on the cylinder head. A comparison of the in-cylinder pressure profiles for diesel fuel and WPBCO at different engine loads, as measured in this study, is shown in Figure 7. It can be seen that the WPBCO has similar in-cylinder pressure profiles when compared to those of diesel fuel, while the peak cylinder pressure for WPBCO and diesel fuel increased continuously as the engine load increased. Additionally, the most important characteristic of a diesel engine is

its peak cylinder pressure, which depends on the initial combustion rate; this is affected by the amount of fuel in the uncontrolled combustion phase, which is controlled by the delay period [46]. The results of this experiment show that the peak cylinder pressure with varying engine loads is lower for WPBCO than for diesel fuel with all engine loads. This may be due to the reduction in the ignition delay caused by the low viscosity and high oxygen content of WPBCO. The low gross calorific value can be also used to explain such a low peak cylinder pressure under the combustion of WPBCO.

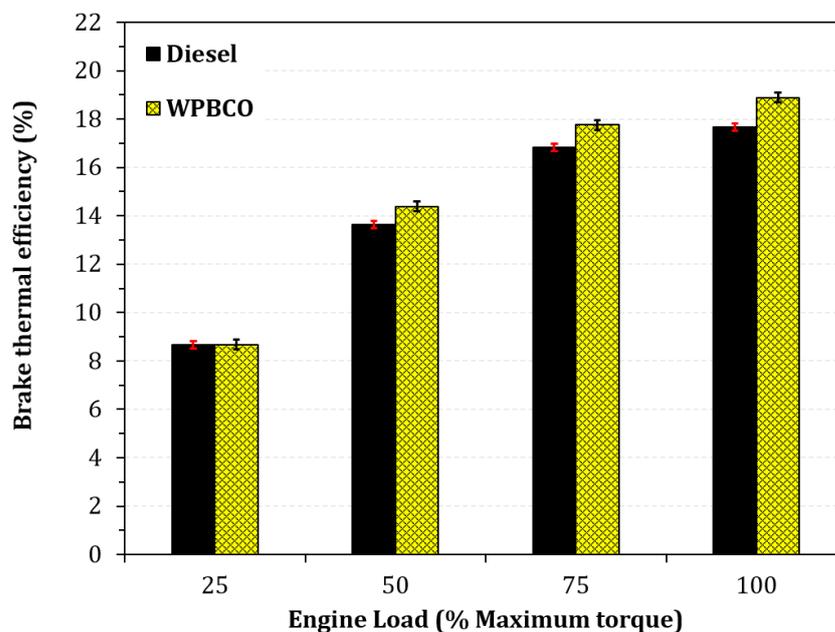


Figure 6. Variation of brake thermal efficiency with respect to engine load.

The RoHR is an important parameter of engine behavior, which helps to describe the combustion characteristics during the burning of fuel in the combustion chamber. The first law of thermodynamics, which was derived from energy conservation, is used to calculate RoHR, along with the combustion products, which were assumed to be ideal gases [37]. The experimental result is shown in Figure 7. It can be seen that the use of WPBCO as an alternative fuel for diesel engines results in a reduction in the ignition delay period at all engine loads, compared to diesel fuel. This is because WPBCO has a low viscosity, which helps to atomize the mixture of air and fuel. This makes the combustion last longer and causes the peak heat release rates to be low [35]. In addition, the higher presence of oxygen in WPBCO can improve fuel oxidation by enhancing ignition quality. It was noted that the low cetane index of WPBCO was compensated by the improvement in ignition quality due to low viscosity and the presence of oxygen; as a result, the combustion characteristics of WPBCO were close to those of diesel fuel, especially when the engine was operated at a high load.

The analysis of variations in the combustion of fuel in the combustion chamber is expressed in terms of the coefficient of variation (COV); this is an undesirable effect that results in reduced engine efficiency and higher exhaust emissions. It also shows the stability of the fuel combustion in each engine cycle. COVPmax is calculated as the ratio of the standard deviation in maximum in-cylinder pressure values to the mean of the maximum in-cylinder pressure for 100 consecutive cycles of engine operation. Figure 8 presents the variation in COVPmax with engine load. The results of cyclic variation showed that the COVPmax decreased as the engine load increased for diesel fuel and WPBCO, which resulted in the stability of brake power output increasing and combustion noise decreasing, while the use of WPBCO led to an increase in the COVPmax values [47]. The main factors contributing to this effect are the chemical composition and fuel properties of WPBCO, which cause unstable combustion. However, the COVPmax values for WPBCO were lower

than 10%, which means the engine was running well and steadily, though it was slightly higher than when it was running on diesel fuel [37].

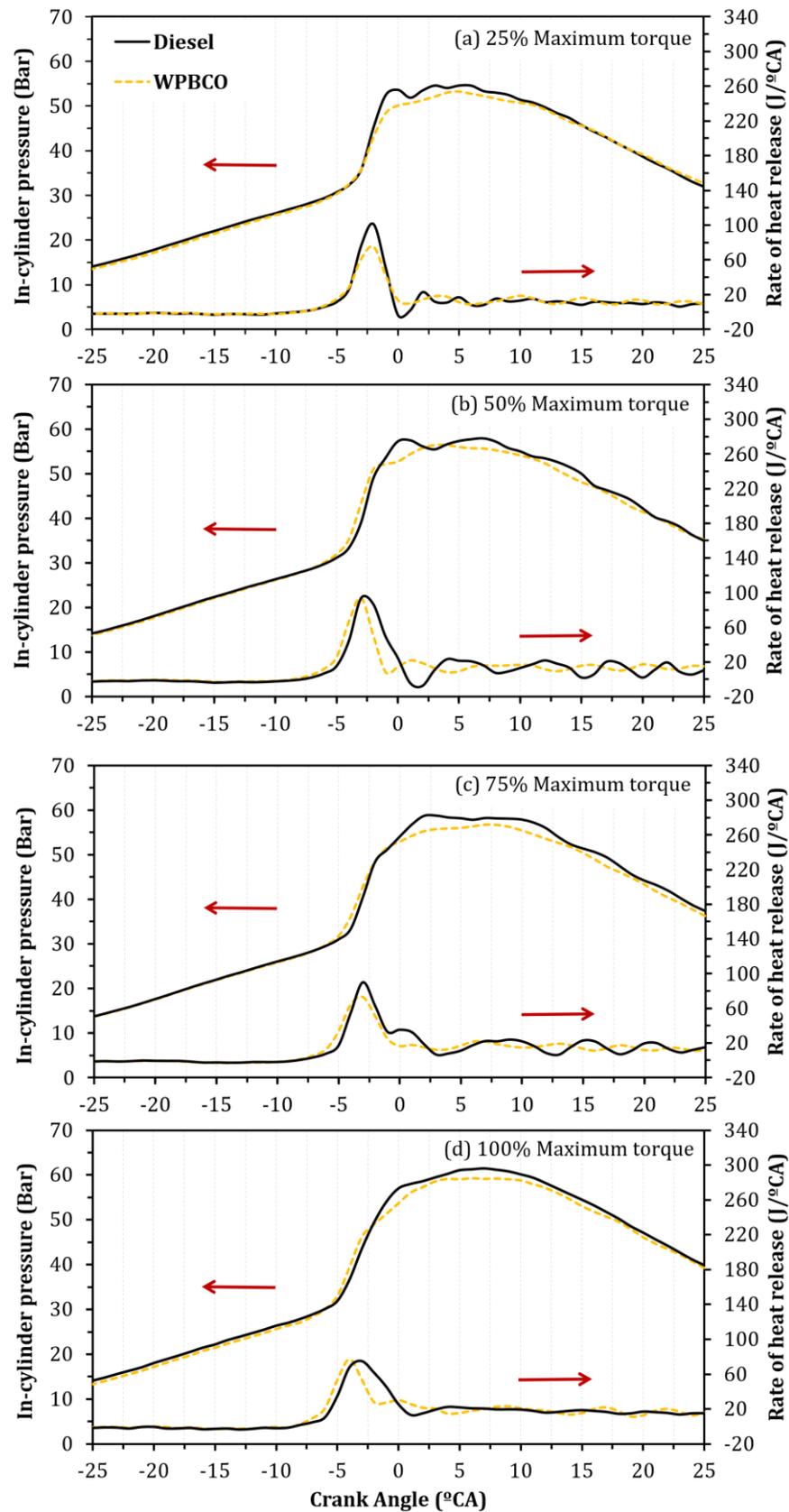


Figure 7. Combustion characteristics under different engine load for diesel fuel and WPBCO.

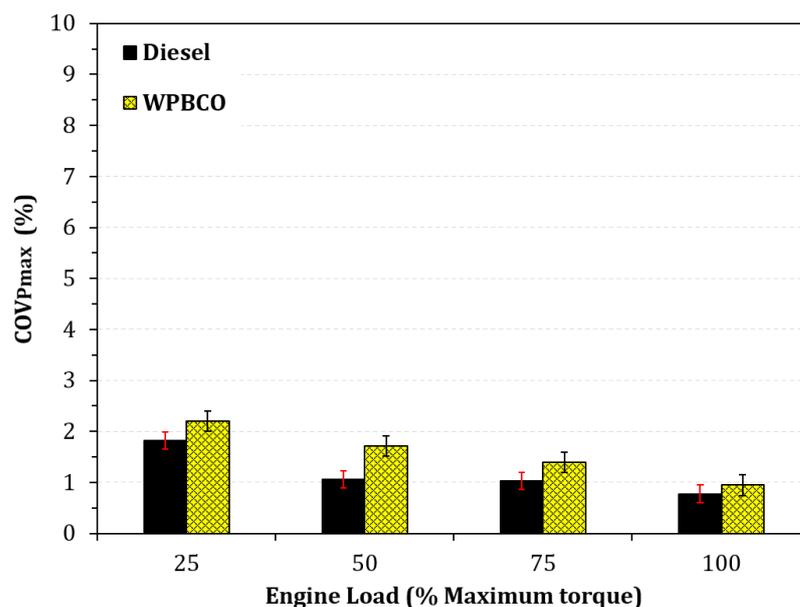


Figure 8. Variation of coefficient of variance in P_{\max} with respect to the engine load.

3.5. Analysis of Emission Characteristics

In this section, the exhaust gas emissions of the diesel engine consisting of nitrogen oxides (NOX), total hydrocarbons (HC), carbon monoxide (CO), and smoke emissions according to engine load operations for diesel fuel and WPBCO are presented and analyzed. The experimental results of the emission characteristics are analyzed as follows:

NOX emissions are the main exhaust gas emissions produced by the combustion of diesel fuel in diesel engines. NOX is caused by the combination of nitric oxide (NO) and nitrogen dioxide (NO₂) produced by the oxidation of nitrogen in the air during the combustion of air and fuel inside the combustion chamber. The generation of NOX in diesel engines is largely dependent on the temperature inside the combustion chamber. The higher the temperature in the combustion chamber, the higher the NOX formation levels. The major mechanisms of NOX formation in diesel engines are the thermal mechanism, the prompt mechanism, and the fuel mechanism [19]. The variation in NOX emissions with increasing engine loads for diesel fuel and WPBCO is shown in Figure 9. For both fuels, there is an increasing trend of NOX emissions when the engine load is increased. This may be due to the high amount of fuel being burned as the engine load increases, which results in a high combustion temperature inside the combustion chamber [48]. Meanwhile, NOX emissions are usually high for WPBCO when compared with diesel fuel. Similar results were obtained by referencing [25,49]. The increment in NOX formation for WPBCO is due to the higher oxygen content in WPBCO compared to diesel fuel [22,50]. Another reason could be that WPBCO has more aromatic compounds than other fuels. This raises the adiabatic flame temperature, which causes large amounts of heat to be released and a lot of NOX to be present in the exhaust [43].

HC emissions refer to the exhaust gas emissions of diesel engines in their gaseous form. HC emissions are formed when incomplete combustion is caused by factors such as an insufficient or abundant air-to-fuel ratio, and they can also result from flame extinction on the walls of the combustion chamber, among other causes. For diesel engines, the level of HC emissions is lower than that of gasoline engines. This is because diesel engines operate at a lean mixture of air and fuel. HC emissions form in the exhaust gas emissions of diesel engines due to flame quenching in the cold regions and poor combustion inside the combustion chamber [51]. The variation in HC emissions with increasing engine loads for both fuels is shown in Figure 10. The results showed that the HC emissions of both fuels increased with the increased engine load operation. When comparing WPBCO and diesel fuel, the HC emissions of WPBCO were higher than those of diesel fuel for all engine loads.

Due to the influence of the high aromatic content, low volatility, and low cetane index of WPBCO compared to diesel fuel, it is difficult to make an air fuel mixture.

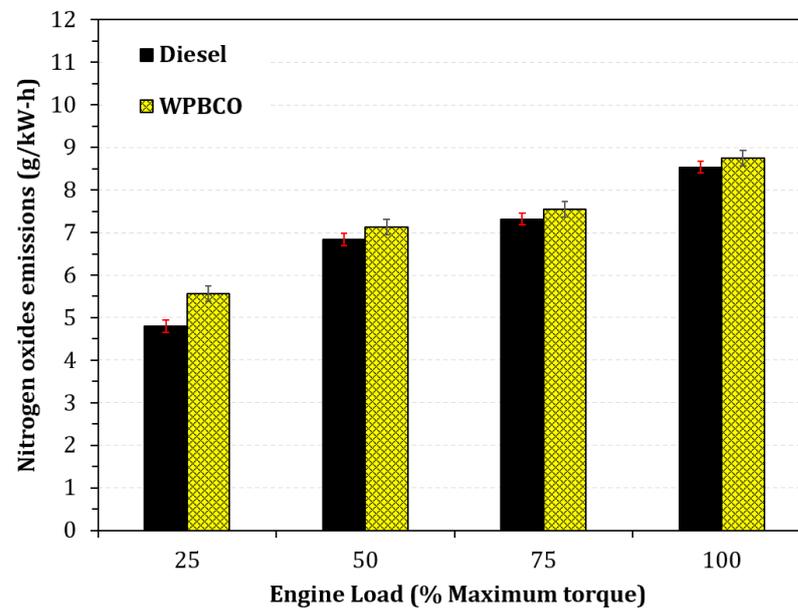


Figure 9. Variation in nitrogen oxide emissions with respect to the engine load.

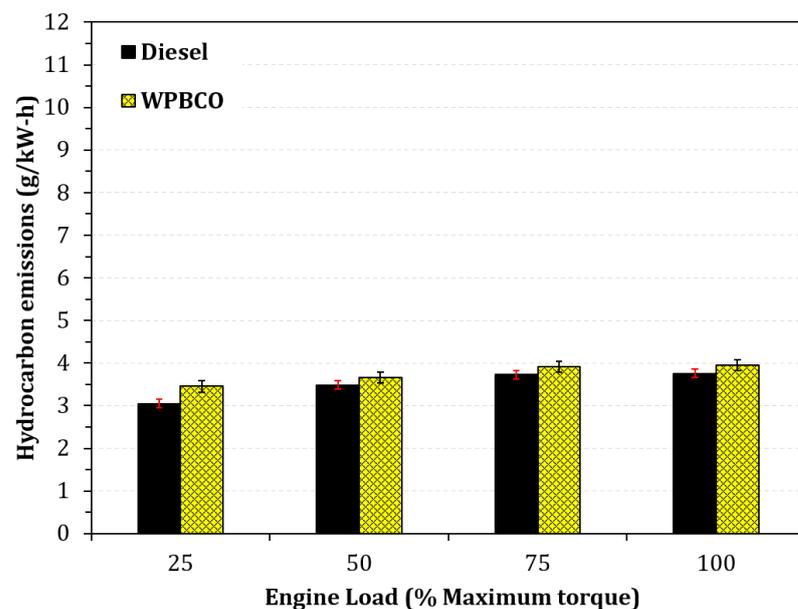


Figure 10. Variation in total hydrocarbon emissions with respect to the engine load.

CO emissions are exhaust gas emission products from the combustion of diesel engines, which are formed due to the incomplete combustion of fuel during the combustion process under the conditions of insufficient oxygen inside the combustion chamber, short burning times, and a poor mixture of air and fuel before combustion. Generally, the CO emissions of diesel engines are low because diesel engines operate with lean mixtures of air and fuel. The variation in CO emissions with increasing engine loads for diesel fuel and WPBCO is shown in Figure 11. It can be seen that the CO emissions of both fuels increase with the increase in engine load operations; the increased load on the engine results in a lower air-to-fuel ratio, higher fuel consumption, and insufficient combustion time [52]. When comparing the test fuels, more CO emissions were obtained with the combustion of WPBCO

compared to diesel fuel for all engine load conditions. This is because WPBCO has less energy and more aromatics than diesel fuel, which makes it burn less well than diesel [21].

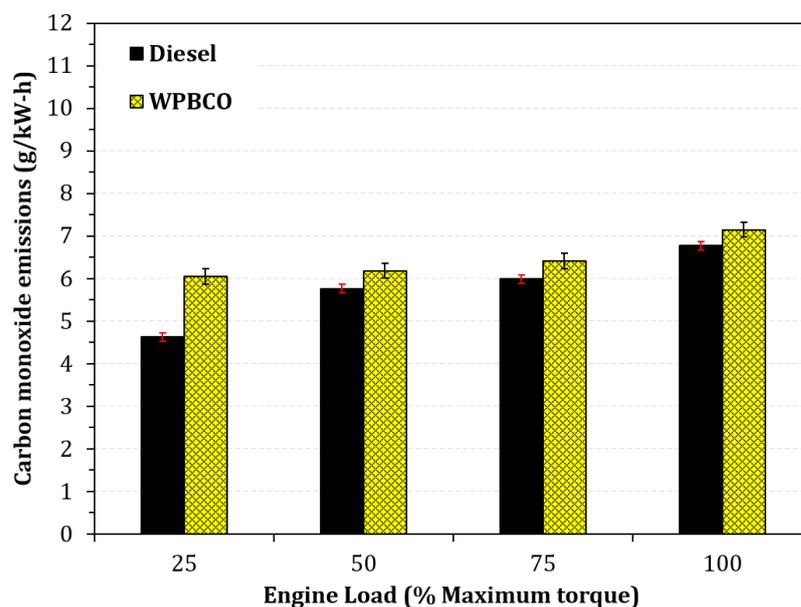


Figure 11. Variation in carbon monoxide emissions with respect to the engine load.

Smoke emissions, which are a visible way to evaluate particulate emissions, represent a solid–liquid phase of carbon particles that are released from the exhaust of diesel engines. In diffusion combustion and pre-combustion flames, such soot is produced by unburned or partially burned fuel. The experimental results of smoke emissions relative to engine loads for diesel fuel and WPBCO are shown in Figure 12. It was observed that the smoke emissions for both fuels increased when the engine load increased, which resulted from the quantity of fuel supplied for every unit time increase [22]. When comparing WPBCO and diesel fuel, the smoke emissions of WPBCO were higher than those of diesel fuel; this may be due to the poor volatility and low energy content in WPBCO, which affect its combustion characteristics. The high amount of aromatics and sulfur compounds in WPBCO also contributes to its high levels of smoke emissions [43]. To reduce the smoke emissions caused by the combustion of WPBCO, the introduction of biodiesel to WPBCO may improve its smoke emissions without requiring any engine modifications. Additionally, desulfurization can be used to remove aromatic sulfur-containing compounds from WPBCO, but the operational cost needs to be considered.

3.6. Analysis of Particulate Matter Characteristics

The analysis of particulate matter (PM) was undertaken by collecting samples of PM generated by the combustion of test fuels in the combustion chamber of the engine, using a fiber glass filter to collect samples under specified conditions. The fiber glass filter sample was weighed to determine the difference in weight before and after the sample was collected. It was also used to analyze the decomposition behavior of PM by using thermogravimetric analysis (TGA) under controlled conditions. The difference in the PM-loaded filter weight obtained with the test fuels is shown in Table 8. It can be seen that the combustion of WPBCO produces higher PM content compared to diesel fuel. This rise in PM emissions is the same as the rise in smoke emissions that comes from burning WPBCO instead of diesel fuel.

In addition, the thermal decomposition of PM for WPBCO and diesel fuel, as shown in Figure 13, produces a first derivative (DTG) curve related to the heating program of TGA. The thermal degradation of PM for both fuels was demonstrated to be between 400 and 600 °C. The rate of soot oxidation of WPBCO occurs within the range of 416–583 °C, with the maximum rate of soot oxidation at 509 °C. The thermal degradation of diesel fuel

occurred at a temperature range of 425–596 °C, and the temperature during the peaks of the decomposition rate was 519 °C. The experimental results indicate that the temperature necessary to reach the maximum rate of soot oxidation was lower with WPBCO combustion than with diesel fuel, indicating that the energy required to oxidize the soot was lower and the soot decomposed more easily [34]. This constitutes a benefit of using WPBCO instead of diesel fuel as a fuel for internal combustion engines.

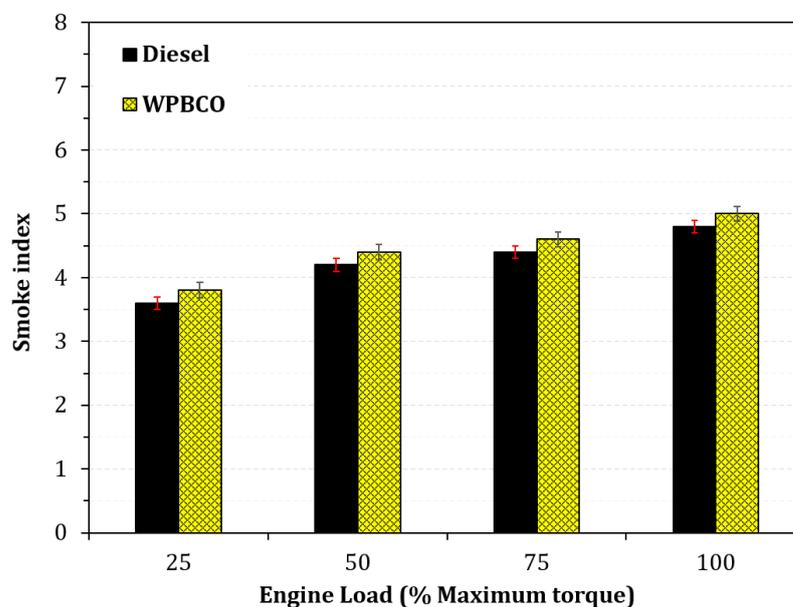


Figure 12. Variation in smoke emissions with respect to the engine load.

Table 8. Difference of PM-loaded filter weight for diesel fuel and WPBCO.

Test Fuels	Weight of Filter Paper (g)		
	Before	After	Percentage
Diesel	0.0901	0.1044	+15.87
WPBCO	0.0923	0.1612	+74.64

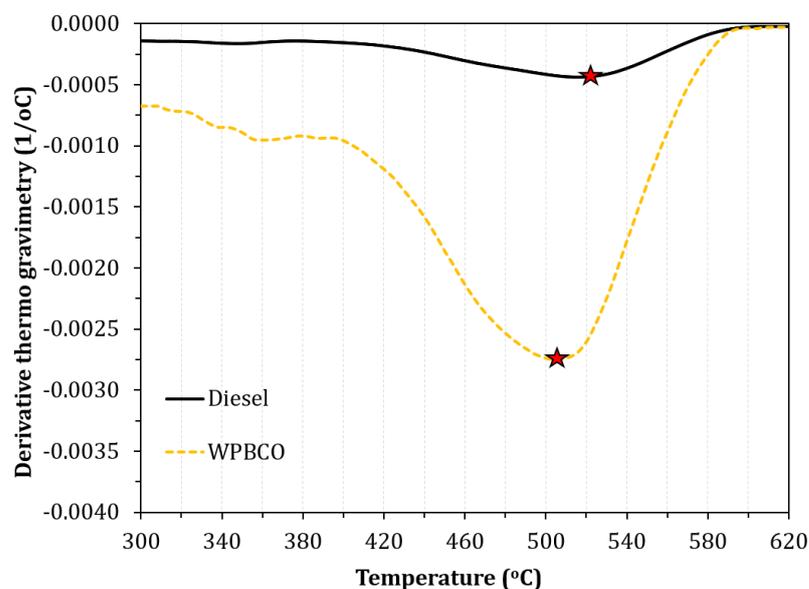


Figure 13. TGA analysis for the PM emissions of diesel fuel and WPBCO at 300–620 °C: red star refers to temperature where the maximum rate of soot oxidation is occurred.

4. Conclusions

In this study, experiments were carried out under varied loads using diesel fuel and pyrolysis oil derived from plastic bottle caps to investigate the effect of pyrolysis oil on the engine and emission characteristics of a diesel engine under different load conditions. The following important conclusions have been drawn from the experimental results:

- Based on the GC–MS results, the components present in different hydrocarbons in WPBCO are mostly alkanes and alkenes with carbon numbers ranging from C₇ to C₂₈. WPBCO has a more complex chemical make-up than diesel fuel. In total, 43.77% of WPBCO is made up of molecules with carbon numbers between C₁₃ and C₁₈, which is the same range as diesel fuel.
- The functional groups of WPBCO were studied and compared with those of diesel fuel. WPBCO had the functional groups C–O stretching (aromatic esters) and C–H stretching (alkenes), but diesel fuel did not. In addition, WPBCO contains carbon (C) and hydrogen (H) as the main constituents that indicate its fuel efficiency. The amounts of carbon and hydrogen for WPBCO are approximately 66.899 wt% and 11.096 wt%, respectively. It has a low energy content. However, it can be used as an alternative fuel.
- Pyrolysis oil derived from plastic bottle caps has the same physical and chemical properties as petroleum fuel, so it can be used as an alternative fuel in diesel engines.
- Using WPBCO in diesel engines resulted in increased BSFC and BTE under all load conditions. It also resulted in decreased ICP, RoHR, and combustion stability.
- The use of WPBCO increased emissions of NO_x, CO, HC, and smoke. This is most likely because WPBCO contains more aromatic sulfur-containing compounds and has lower volatility, a lower cetane index, and lower calorific value than diesel fuel.
- An analysis of PM revealed that WPBCO had a higher PM concentration than diesel fuel, mainly because of the higher amount of aromatic sulfur-containing compounds that are primary components of PM formation. However, the temperature necessary to reach the maximum rate of soot oxidation was lower for WPBCO combustion than for diesel fuel.
- To achieve a reduction in engine-out emissions, the addition of biodiesel to WPBCO and the use of a cetane improver may improve the combustion of WPBCO without requiring any engine modifications; this possibility can be considered in future studies.

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