

Utilizing Waste Plastic Bottle-Based Pyrolysis Oil as an Alternative Fuel

Somkiat Maithomklang, Khatha Wathakit, Ekarong Sukjit, Boonlue Sawatmongkhon, and Jiraphon Srisertpol*



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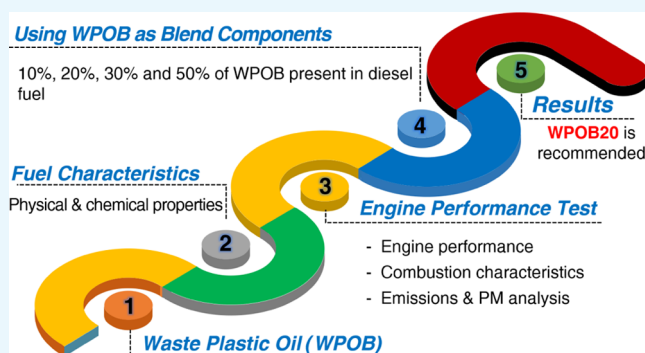
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ABSTRACT: In the present work, an experimental investigation is carried out on the use of waste plastic oil produced from waste poly(ethylene terephthalate) (PET) bottles (WPOB) as an alternative fuel for diesel engines. The physical and chemical properties of WPOB were analyzed, and it was found that it has fuel properties similar to those of petroleum fuels. The WPOB was tested in a diesel engine to evaluate the effect of WPOB on combustion and emissions characteristics. In addition, particulate matter (PM) emissions generated by the combustion of WPOB were analyzed. The combustion of WPOB was retarded with respect to diesel fuel, resulting in higher carbon-based emissions. The thermogravimetric analysis (TGA) results show that the temperature to reach the maximum rate of soot oxidation was lower with WPOB combustion. Because of the significant delay at the start of combustion and increase in emissions, the direct use of WPOB in the diesel engine is not recommended. It is suggested that WPOB can be used as a blend component to reduce the amount of diesel fuel used in diesel engines. Thus, further study on the effect of diesel fuel blended with WPOB on the combustion and emissions characteristics was performed. The results reveal that the maximum WPOB present in diesel fuel to avoid the increase in carbon-based emissions is 20% by volume to keep combustion and emissions characteristics similar to those of diesel fuel.



1. INTRODUCTION

Thailand has been facing the problem of environmental pollution, especially in the form of the huge amount of plastic waste, which increased manifold during the Covid-19 pandemic due to the increased use of plastic products resulting from online food delivery and take-away packaging during this period. This results in a significant impact on human health and causes environmental pollution due to the fact that plastic waste cannot be degraded by natural organisms and requires hundreds of years for decomposition. This situation results in a high quantity of plastic waste. According to the Pollution Control Department of Thailand Report, plastic waste of approximately two million tons was generated in 2020, which is about 12% of the total municipal solid waste (MSW) by weight.^{1–3} Plastic materials like poly(ethylene terephthalate) (PET) are widely used for beverage packaging (especially drinking water and soft drinks) due to their excellent combination of properties, which make them suitable for containers. The extensive use of plastic PET bottles causes a high quantity of collected PET waste in landfills.⁴ In addition, waste PET bottles comprise one of the municipal plastic waste components. Currently, the amount of plastic PET bottles used in Thailand amounts to more than 4000 million bottles per year. Therefore, a waste management

technique is necessary to address the plastic waste problem, which includes reducing, reusing, recycling, recovering, and disposal. In fact, only 0.5 million ton could be recovered for recycling, while the remaining plastic waste containers eventually ended up in landfills. This situation originates from an ineffective management system.⁵ The technique of energy recovery from plastic waste is of great interest in converting waste to fuel for energy resources since it can help decrease the plastic waste problem and rehabilitate the environment in Thailand.

According to the literature review, many researchers have studied the use of plastic waste in fuel production as an alternative fuel in compression ignition (CI) engines. This is because plastic waste is a petrochemical product that contains mainly carbon and hydrogen atoms and has a high energy content.^{4,6,7} Fuel produced from plastic waste can be extracted

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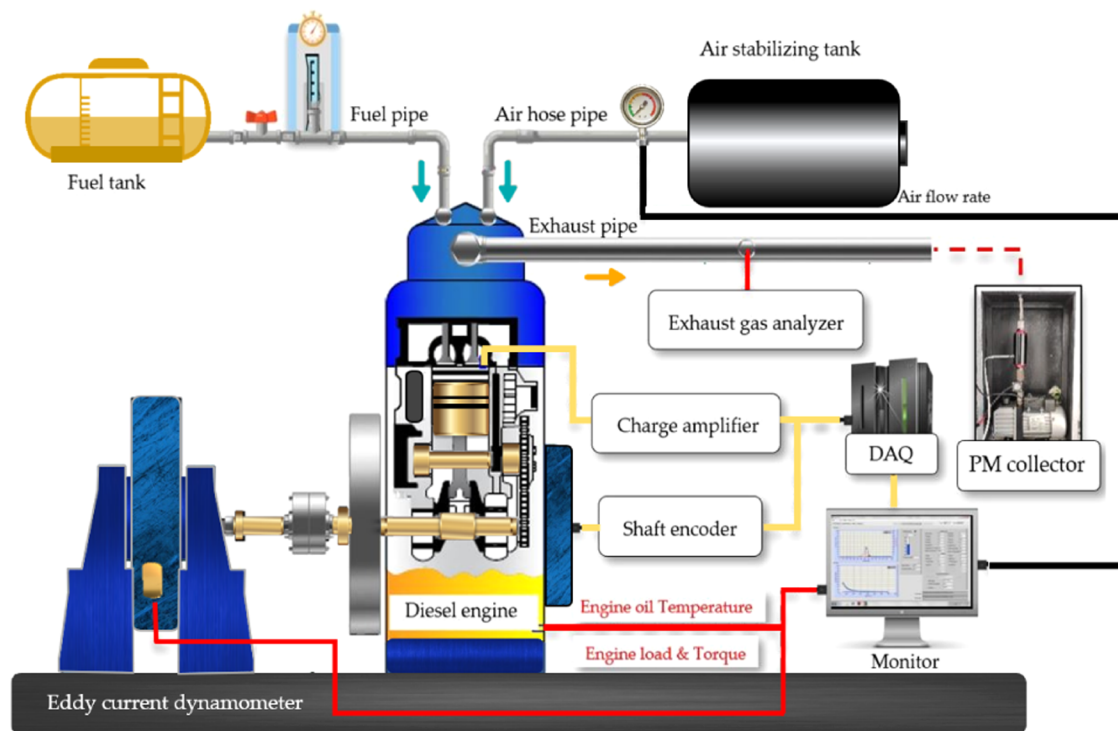


Figure 1. Schematic diagram of the experimental setup.

by the pyrolysis process, which is the most appropriate technology to convert polymer waste into fuel. Previous research had found that the fuel characteristic of waste plastic oil (WPO) was similar to that of diesel fuel,⁸ notably, the physical and chemical property characteristics of WPO, depending on the feedstock type and pyrolysis process parameters (e.g., reaction temperature, pressure, residence time, heating rate, and type of catalyst). Sharuddin et al.⁹ reported the production of fuel derived from the pyrolysis process for various plastic waste types including polystyrene (PS), polypropylene (PP), high-density polyethylene (HDPE), low-density polyethylene (LDPE), poly(vinyl chloride) (PVC), poly(ethylene terephthalate) (PET), and mixed plastics. It can be concluded that the plastic type influenced the characteristic and quality of the fuel produced due to its difference in composition.

On the other hand, the experimental result of many investigators demonstrated that the utilization of WPO in diesel engines exhibited an increasing trend in brake-specific fuel consumption (BSFC) and brake thermal efficiency (BTE) when compared with those of diesel fuel. However, the exhaust emissions resulting from the combustion of WPO, including nitrogen oxides (NO_x), unburnt hydrocarbon (HC), carbon monoxide (CO), and smoke emission, tend to increase with the use of WPO. In addition, WPO has significant influences on combustion characteristics of the engine, wherein the use of WPO leads to an increase in the ignition delay period along with an increased rate of heat release (RoHR) and in-cylinder pressure (ICP), which are important parameters in the combustion characteristics of CI engines.^{10,11} However, some researchers found that the engine performance using WPO as a fuel in CI engines was higher than when using diesel fuel along with a reduction in NO_x , CO, and smoke emissions. This is due to the chemical compounds in WPO.^{12–16} Furthermore, characteristics of particulate matter (PM) emissions caused by the combustion of alternative fuel in CI engines were also

investigated for an explanation of PM compositions. Adam et al.¹⁷ characterized volatile matters and soot as compositions of PM of waste source fuel by thermogravimetric analysis (TGA), which characterizes volatile matters and soot as compositions of PM by monitoring the mass loss with temperature increase. Therefore, the TGA technique is particularly interesting for the PM emission analysis of diesel engines operating with WPO.

The purpose of this research is to study the possibility of the use of waste plastic oil (WPOB) derived from the pyrolysis of waste poly(ethylene terephthalate) (PET) bottles as an alternative fuel for replacing fossil diesel fuel used in CI engines. Its effects on engine performance, combustion characteristics, and exhaust gas emissions were analyzed. Moreover, the soot oxidation temperature of PM generated by the combustion of WPO was also investigated.

2. MATERIALS AND METHODS

2.1. Preparation of the Test Fuel and Its Characterization. The waste plastic oil (WPOB) used in this study was produced from waste plastic bottles (PET bottles) using the pyrolysis process, which is a thermochemical degradation reaction at high temperatures to decompose plastics in the absence of oxygen or a low-oxygen environment to produce liquid and gaseous fuel. The experiment was carried out in a laboratory at Suranaree University of Technology, Thailand. The waste PET bottles were reduced in size by cutting into smaller pieces of around 1 cm^2 . The reactor was loaded with about 1000 g of waste PET bottles with 25 g of CaSiO_2 catalyst. The pyrolysis process was carried out using a small fixed-bed reactor. It was heated to reach a temperature of about $450 \text{ }^\circ\text{C}$, using a heating rate of $15 \text{ }^\circ\text{C}/\text{min}$ and a reaction time of 30 min.¹⁸ The products of this process are gas vapor, and these products go through a condenser to produce liquid fuel (waste plastic oil). These conditions produce a yield of an average of 70–80% of crude oil and 20–30% of solid residue. The diesel

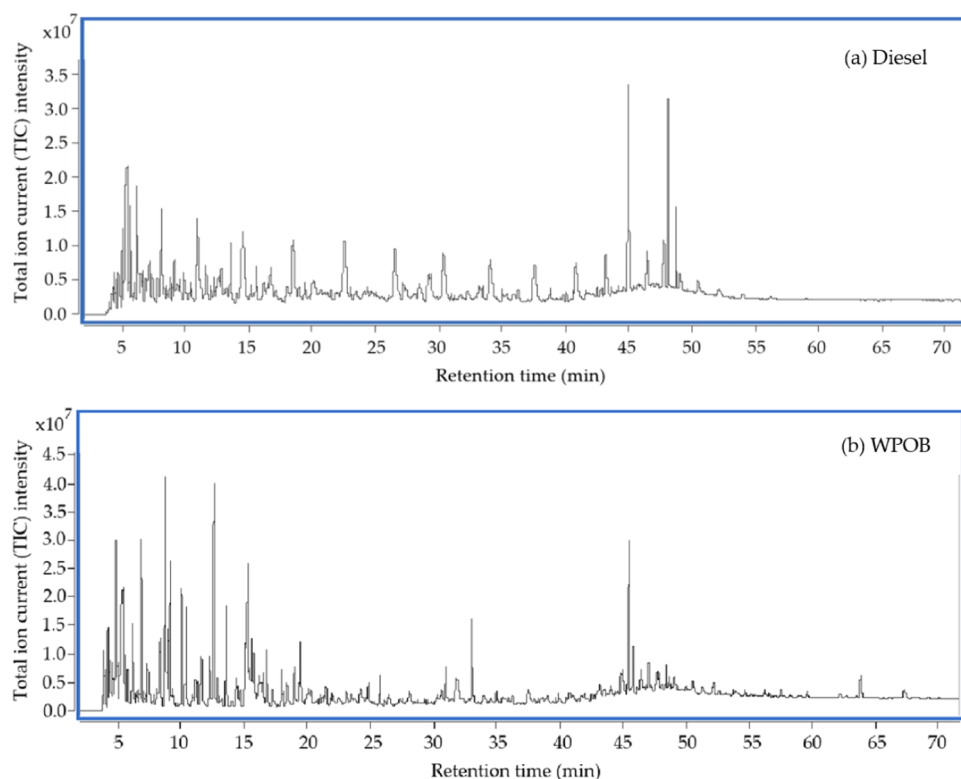


Figure 2. GC–MS chromatogram results for (a) diesel and (b) WPOB.

fuel used as a baseline fuel was a commercial-grade one available in public fuel stations (blends of 7% biodiesel, mainly using crude palm oil as the feedstock). The physical and chemical properties of test fuels were measured according to the American Society for Testing and Materials (ASTM) standard. The chemical compound and functional group of WPOB and the diesel fuel were characterized by gas chromatography–mass spectrometer (GC–MS) and Fourier transform infrared spectroscopy (FT-IR) techniques.

2.1.1. Chemical Characteristic Analysis of the Test Fuel. The chemical compound and functional group were obtained by GC–MS and FT-IR techniques. GC–MS is a chemical analysis instrument for separation and identification at the molecular level of chemical composition in a complex chemical mixture of the produced fuel. The test fuels used in this study were characterized by GC–MS using an Agilent Technologies 7890A coupled to an Agilent Technologies 7693 ALS mass selective detector. The techniques of GC–MS used for the analysis have been detailed in ref 19. FT-IR is a technique that is used to recognize the various characteristic functional groups present in the produced fuel. Upon interaction of infrared light with the produced fuel, chemical bonds can absorb infrared radiation in specific wavelength ranges regardless of the structure of the rest of the molecules. FT-IR analysis of the test fuels was performed using Bruker (TENSOR27-Hyperion) and was scanned in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1} . Moreover, elemental analysis of test fuels was analyzed by a CHNS elemental analyzer (LECO CHN628/628S) to investigate the carbon, hydrogen, nitrogen, and sulfur contents of the fuels.

2.1.2. Physical and Chemical Properties of Test Fuels. The investigation of the physical and chemical properties is very important for the possible application as an alternative fuel in internal combustion engines (ICEs). The results showed that the physical and chemical properties of the test fuels assessed

corresponded to the ASTM standard. The physical and chemical properties of test fuels used in this study, such as kinematic viscosity, specific gravity, density, flash point, fire point, gross calorific value, cetane index, and distillation temperature, were compared to those of diesel fuel. In addition, the lubricity of test fuels was evaluated using a high-frequency reciprocating rig (HFRR). The test conditions were based on the ASTM D6079 standard.²⁰

2.2. Experimental Setup and Procedure for the Engine Test. The experimental investigation was performed to evaluate and compare the result of the engine performance, combustion characteristics, and emissions of WPOB with diesel fuel. A single-cylinder, four-stroke, and water-cooled DI diesel engine with a rate power of 3.5 kW at 1500 rpm was used.¹⁹ The engine load was accomplished using a water-cooled eddy current dynamometer. The experimental setup is shown in Figure 1.

The engine was operated at a constant speed of 1500 rpm and at three different engine operating loads of 25, 50, and 75% of the maximum engine torque conditions for all test fuels. The fuel consumption was measured on a volumetric basis with the help of a burette and using a digital stopwatch (resolution of 0.01 s). Meanwhile, the in-cylinder pressure was measured by a PCB piezotronics pressure sensor mounted on the cylinder head connected to a charge amplifier to a data acquisition board (DAQ). The Kubler crank angle sensor was used to detect the engine crank angle during the combustion process of the engine. EngineSoft software was used to analyze the combustion characteristics of the engine. The exhaust gas emissions comprising unburned hydrocarbons (HCs), carbon monoxide (CO), and nitrogen oxides (NO_x) were measured with a gas analyzer (Testo 350 flue gas analyzer), which measures HC emissions by the flame ionization detector (FID), CO emissions by the nondispersive infrared (NDIR) method, NO_x emissions by the chemiluminescence method, and smoke emissions in the

exhaust gas with the photodiode (filter paper) method (Testo 308 smoke meter). The technical details of the exhaust gas analyzers are presented in ref 19.

For the test condition, the engine was first warmed up with the test fuel with no engine load until the engine oil temperature reached 70 °C, indicating that the engine was ready for collecting the data. Also, the values of all test parameters were replicated three times, and the values were taken on average to ensure the reproducibility of experimental data. The experimental data was provided using the confidence interval, which was considered statistically significant with a 95% confidence level to consider the trends of the results.

2.3. Experimental Setup and Procedure for Particulate Matter (PM) Analysis. Particulate matter (PM) characteristics produced during the combustion process of test fuels were investigated under the same conditions. PM was collected using a PM collector, as equipped with an exhaust pipe of the diesel engine, with a constant exhaust gas flow rate of 15 L/min. The time for loading PM on the filter paper was 30 min, and the engine was operated at a constant speed of 1500 rpm and 50% engine load. The Whatman glass microfiber filter paper-grade GF/C (47 mm diameter, with 1.2 micron pore size) was used to load PM caused by the combustion of test fuels. An analytical balance (Sartorius BP221S) was used to evaluate the weight of the PM emissions loaded on the filter paper by weighing the filter paper before and after the PM collection. Thermogravimetry (TGA) analysis (Mettler Toledo, TGA/DSC1) was applied to characterize soot as the composition of PM. All samples of the PM-loaded filter were cut into small pieces of about 5 mm², and the weight of PM collected on the loaded filter used for TGA was in the range of 2.0–5.0 mg, which was placed into the sample basket of the thermogravimetric analyzer for heating in the TGA according to the following program. The first step in the heating program is the initial atmosphere of oxygen with a constant flow rate of 60.0 mL/min. In the second step, the PM-loaded filter was heated from 35 to 110 °C at a heating rate of 5.00 °C/min under an oxygen atmosphere. Then, the temperature was kept at 110 °C for 5 min. The PM-loaded filter was heated up again from 110 to 700 °C at a heating rate of 5.00 °C/min under an oxygen atmosphere. Finally, the temperature was kept at 700 °C for 5.00 min.

3. RESULTS AND DISCUSSION

3.1.. Analysis of Gas Chromatography–Mass Spectrometry. The quantitative analysis of test fuels by GC–MS based on the percentage of peak results, which was calculated from the total ion current (TIC) area, is presented in Figure 2. The identified compounds present in diesel fuel are shown in Table 1. The GC–MS analysis was performed for each batch under identical pyrolysis operating conditions to ensure its reproducibility for chemical composition in waste plastic oil produced from waste PET bottles, and the chemical compositions are shown in Table 2. The chemical composition of fuels is very complicated because they contain different types of compounds. Nevertheless, the results shown in Table 2 indicate that the average molecular weight of WPOB was 186.52 g/mol, which was lower than that of diesel fuel (229.99 g/mol), and its chemical compounds distributed in the hydrocarbon compounds range of C₆–C₂₆ with a H/C molar ratio of 1.758, which is close to the range of petroleum fuel. Moreover, the main hydrocarbon compounds present in WPOB were in a group of C₆–C₁₂, as presented in Table 3, and commonly contain major chemical compounds of benzene, ethylbenzene, heptane,

Table 1. Identified Compounds Present in Diesel Fuel

compound name	chemical information		
	area (%)	formula	MW
octane	0.78	C ₈ H ₁₈	114.14
cyclohexane, 1,4-dimethyl-	0.82	C ₈ H ₁₆	112.12
nonane	1.67	C ₉ H ₂₀	128.15
nonane, 4-methyl-	1.61	C ₁₀ H ₂₂	142.17
decane	3.62	C ₁₀ H ₂₂	142.17
undecane	4.18	C ₁₁ H ₂₄	156.18
<i>p</i> -xylene	0.94	C ₈ H ₁₀	106.07
<i>trans</i> -2-dodecen-1-ol	1.09	C ₁₂ H ₂₄ O	184.18
dodecane	5.99	C ₁₂ H ₂₆	170.20
benzene, 1-ethyl-3-methyl-	0.92	C ₉ H ₁₂	120.09
benzene, 1,2,3-trimethyl-	1.62	C ₉ H ₁₂	120.09
tridecane	6.39	C ₁₃ H ₂₈	184.21
benzene, 1,2,4-trimethyl-	1.40	C ₉ H ₁₂	120.09
tetradecane	6.52	C ₁₄ H ₃₀	198.23
1-tetradecene	1.57	C ₁₄ H ₂₈	196.21
pentadecane	5.66	C ₁₅ H ₃₂	212.25
hexadecane	5.95	C ₁₆ H ₃₄	226.26
heptadecane	5.69	C ₁₇ H ₃₆	240.28
octadecane	4.30	C ₁₈ H ₃₈	254.29
nonadecane	4.01	C ₁₉ H ₄₀	268.31
eicosane	3.90	C ₂₀ H ₄₂	282.32
heneicosane	3.19	C ₂₁ H ₄₄	296.34
hexadecanoic acid, methyl ester	10.11	C ₁₇ H ₃₄ O ₂	270.25
tricosane	2.36	C ₂₃ H ₄₈	324.37
methyl stearate	2.06	C ₁₉ H ₃₈ O ₂	298.28
11-octadecenoic acid, methyl ester	7.59	C ₁₉ H ₃₆ O ₂	296.27
linoleic acid, methyl ester	2.45	C ₁₉ H ₃₄ O ₂	294.25
pentacosane	1.19	C ₂₅ H ₅₂	352.40
hexacosane	1.13	C ₂₆ H ₅₄	366.42
heptacosane	0.62	C ₂₇ H ₅₆	380.43
octacosane	0.34	C ₂₈ H ₅₈	394.45
nonacosane	0.33	C ₂₉ H ₆₀	408.46

toluene, and xylene, which represent light hydrocarbons similar to gasoline fuel,²¹ while diesel fuel was found to possess a high hydrocarbon content of approximately 46.18% in the hydrocarbon compound range of C₁₃–C₁₈.

The FT-IR spectra of diesel fuel and WPOB are shown in Figure 3. The FT-IR spectra results showed that similar main peaks of FT-IR spectra were seen for WPOB compared to that of the diesel fuel, which indicated similar functional groups for both fuels. The main peaks were observed at the wavelengths of 2954, 2922, 2853, 1746, 1605, 1460, and 722 cm⁻¹ for diesel fuel. The presence of a large intense bond was observed for C–H stretching at 2954, 2922, and 2853 cm⁻¹; C=O stretching at 1746 cm⁻¹; C–H bending at 1605 and 1460 cm⁻¹; and C=C bending at 722 cm⁻¹. The FT-IR spectra of WPOB show the C–H stretching at 2956, 2923, and 2855 cm⁻¹; C=O stretching at 1720 cm⁻¹; C–H bending at 1456 and 1377 cm⁻¹; C=C bending at 887 cm⁻¹; and C–Br stretching at 697 cm⁻¹. The results of both fuels indicated that the diesel fuel shows the presence of mostly alkene and alkane compounds, while the presence of aromatics with some alkenes and alkanes was observed for WPOB, which further confirmed the GC–MS results.²²

Carbon (C) and hydrocarbon (H) contents are the parameters for the quality of fuel. The results obtained after the elemental analysis results of WPOB and diesel fuel are shown in Table 4. It shows that C and H contents of diesel fuel are

Table 2. Identified Compounds Present in Waste Plastic Oil Produced from PET Bottles

compound name	area (%)			chemical information	
	batch 1	batch 2	batch 3	formula	MW
cyclohexane	0.87	0.00	0.00	C ₆ H ₁₂	84.09
heptane	0.84	0.00	0.00	C ₇ H ₁₆	100.12
heptane, 4-methyl-	1.63	1.25	1.25	C ₈ H ₁₈	114.14
heptane, 2,4-dimethyl-	1.07	5.92	5.83	C ₉ H ₂₀	128.15
2,3-dimethyl-3-heptene	6.57	0.00	0.00	C ₉ H ₁₈	126.14
nonane, 4-methyl-	0.60	0.00	0.00	C ₁₀ H ₂₂	142.17
6,6-dimethylhepta-2,4-diene	0.46	0.00	0.00	C ₉ H ₁₆	124.12
cyclohexene, 3,3,5-trimethyl-	0.53	0.00	0.00	C ₉ H ₁₆	124.12
octane, 3,5-dimethyl-	2.10	0.00	0.00	C ₁₀ H ₂₂	142.17
toluene	5.10	3.50	3.53	C ₇ H ₈	92.06
acetic acid, butyl ester	0.82	0.00	0.00	C ₆ H ₁₂ O ₂	116.08
undecane	0.58	0.00	0.00	C ₁₁ H ₂₄	156.18
1-decene, 2,4-dimethyl-	2.04	0.00	0.00	C ₁₂ H ₂₄	168.18
ethylbenzene	8.59	11.40	11.96	C ₈ H ₁₀	106.07
<i>o</i> -xylene	2.25	0.00	0.00	C ₈ H ₁₀	106.07
<i>p</i> -xylene	3.75	0.00	0.00	C ₈ H ₁₀	106.07
benzene, (1-methylethyl)-	3.16	3.19	3.22	C ₉ H ₁₂	120.09
<i>m</i> -xylene	2.43	2.16	2.12	C ₈ H ₁₀	106.07
benzene, propyl-	0.85	0.00	0.00	C ₉ H ₁₂	120.09
1-methoxy-2-propyl acetate	0.63	0.00	0.00	C ₆ H ₁₂ O ₃	132.07
benzene, 1-ethyl-4-methyl-	1.30	2.32	2.27	C ₉ H ₁₂	120.09
benzene, 1,2,4-trimethyl-	1.35	0.00	0.00	C ₉ H ₁₂	120.09
styrene	7.38	7.83	8.01	C ₈ H ₈	104.06
benzene, 1-ethyl-2-methyl-	0.64	0.00	0.00	C ₉ H ₁₂	120.09
benzene, 1,2,3-trimethyl-	3.01	3.28	3.28	C ₉ H ₁₂	120.09
benzene, 1-methyl-3-propyl-	0.96	2.25	2.23	C ₁₀ H ₁₄	134.10
α -methyl styrene	4.94	6.69	6.49	C ₉ H ₁₀	118.07
benzene, 1,2,4-trimethyl-	2.20	0.00	0.00	C ₉ H ₁₂	120.09
benzene, 2-ethyl-1,4-dimethyl-	0.85	2.17	2.11	C ₁₀ H ₁₄	134.10
benzene, 1-ethyl-3,5-dimethyl-	1.08	0.00	0.00	C ₁₀ H ₁₄	134.10
benzene, 1-ethyl-2,4-dimethyl-	1.62	2.38	2.31	C ₁₀ H ₁₄	134.10
ethanol, 2-butoxy-	0.99	0.00	0.00	C ₆ H ₁₄ O ₂	118.09
benzene, 1-ethyl-2,3-dimethyl-	0.76	0.00	0.00	C ₁₀ H ₁₄	134.10
benzene, 1,2,4,5-tetramethyl-	1.08	0.00	0.00	C ₁₀ H ₁₄	134.10
benzene, 1,2,3,4-tetramethyl-	2.23	3.51	3.48	C ₁₀ H ₁₄	134.10
benzene, (3-methyl-3-butenyl)-	0.52	0.00	0.00	C ₁₁ H ₁₄	146.10
benzene, 4-ethenyl-1,2-dimethyl-	0.35	0.00	0.00	C ₁₀ H ₁₂	132.09
benzene, 1,2,3,5-tetramethyl-	0.59	0.00	0.00	C ₁₀ H ₁₄	134.10
benzene, heptyl-	0.69	0.00	0.00	C ₁₃ H ₂₀	176.15
hexadecane	0.00	1.34	1.41	C ₁₆ H ₃₄	226.27
benzotrile	0.80	0.00	0.00	C ₇ H ₅ N	103.04
naphthalene	1.02	2.19	2.11	C ₁₀ H ₈	128.06
1-decanol, 2-hexyl-	2.07	0.00	0.00	C ₁₆ H ₃₄ O	242.26
heptadecane	0.00	1.37	1.36	C ₁₇ H ₃₆	240.28
octadecane	0.00	1.76	1.71	C ₁₈ H ₃₈	254.30
ethanol, 1-(2-butoxyethoxy)-	2.42	2.63	2.60	C ₈ H ₁₈ O ₃	162.12
ethanol, 2-(2-butoxyethoxy)-, acetate	0.24	0.00	0.00	C ₁₀ H ₂₀ O ₄	204.13
naphthalene, 2-methyl-	0.34	0.00	0.00	C ₁₁ H ₁₀	142.07
nonadecane	1.05	1.28	1.26	C ₁₉ H ₄₀	268.31
eicosane	0.00	2.52	2.52	C ₂₀ H ₄₂	282.33
heneicosane	0.00	2.59	2.64	C ₂₁ H ₄₄	296.34
phenol, 2-(1-methylethyl)-	0.29	0.00	0.00	C ₉ H ₁₂ O	136.08
docosane	1.69	2.57	2.56	C ₂₂ H ₄₆	310.36
benzene, 1,1'-(1,3-propanediyl)bis-	0.00	6.56	6.57	C ₁₅ H ₁₆	196.13
1,3-diphenylbutane	0.46	0.00	0.00	C ₁₆ H ₁₈	210.14
1,3-diphenylpropane	3.14	0.00	0.00	C ₁₅ H ₁₆	196.12
<i>N</i> -methyl phthalimide	0.66	0.00	0.00	C ₉ H ₇ NO ₂	161.04
tricosane	0.95	1.84	1.84	C ₂₃ H ₄₈	324.37
1,4-diphenylbutane	0.53	0.00	0.00	C ₁₆ H ₁₈	210.14

Table 2. continued

compound name	area (%)			chemical information	
	batch 1	batch 2	batch 3	formula	MW
tetracosane	1.02	2.70	2.67	C ₂₄ H ₅₀	338.39
18-norabieta-8,11,13-triene	0.54	0.00	0.00	C ₁₉ H ₂₈	256.21
α -N-normethadol	0.49	0.00	0.00	C ₂₀ H ₂₇ NO	297.20
pentacosane	0.63	2.07	2.03	C ₂₅ H ₅₂	352.41
hexacosane	0.78	1.83	1.89	C ₂₆ H ₅₄	366.42
heptacosane	0.00	1.04	1.04	C ₂₇ H ₅₆	380.44
naphthalene, 1-phenyl-	0.38	0.00	0.00	C ₁₆ H ₁₂	204.09
octacosane	0.00	1.48	1.44	C ₂₈ H ₅₈	394.45
nonacosane	0.00	0.59	0.57	C ₂₉ H ₆₀	408.47
anthracene, 2-methyl-	0.41	0.00	0.00	C ₁₅ H ₁₂	192.09
naphthalene, 2-phenyl-	0.29	0.94	0.91	C ₁₆ H ₁₂	204.09
triacontane	0.00	0.69	0.68	C ₃₀ H ₆₂	422.49
phenanthrene, 3,6-dimethyl-	0.26	0.80	0.79	C ₁₆ H ₁₄	206.10
9-phenyl-5H-benzocycloheptene	0.18	0.00	0.00	C ₁₇ H ₁₄	218.10
retene	1.25	3.36	3.32	C ₁₈ H ₁₈	234.14
1-acetyl-20 α -hydroxy-16-methylene-	0.69	0.00	0.00	C ₂₁ H ₂₆ N ₂ O ₂	338.19

Table 3. Range of Hydrocarbon and Carbon Number Distribution of WPOB and Diesel Fuel

carbon number distribution	percentage of area	
	diesel	WPOB
C ₆ –C ₁₂ (gasoline/light fraction)	24.65	69.33 \pm 11.40
C ₁₃ –C ₁₈ (diesel/middle fraction)	46.18	13.95 \pm 3.72
C ₁₉ –C ₂₃ (fuel oil/middle fraction)	25.56	9.01 \pm 3.11
>C ₂₄ (residual fuel/heavy fraction)	3.61	7.71 \pm 4.58

83.230 and 11.020 wt %, respectively, while C and H contents of WPOB are 80.740 and 11.912 wt %, respectively. This carbon content was also lower with respect to diesel fuel, which indicates a low energy content when compared to diesel fuel. Moreover, the sulfur (S) content is high in WPOB, making it unsuitable for use as a fuel in compression ignition engines, resulting in increased SO_x emissions.²³

Table 4. Elemental Analyses of Diesel Fuel and WPOB

elements	composition (wt %)	
	diesel	WPOB
carbon (C)	83.230	80.740
hydrogen (H)	11.020	11.912
nitrogen (N)	0.018	
sulfur (S)	0.000	0.769

3.2. Analysis of Fuel Properties. The results of physical and chemical properties are shown in Table 5. It can be indicated that the kinematic viscosity of WPOB was comparably lower than that of diesel fuel, and these values were lower than the minimum value for the diesel fuel standard due to the lower molecular weight of WPOB, resulting in a lower viscosity.²⁴ The specific gravity and density for WPOB are 0.825 and 824 kg/m³, respectively. These values were also lower with respect to those of diesel fuel. These properties are associated with the efficiency

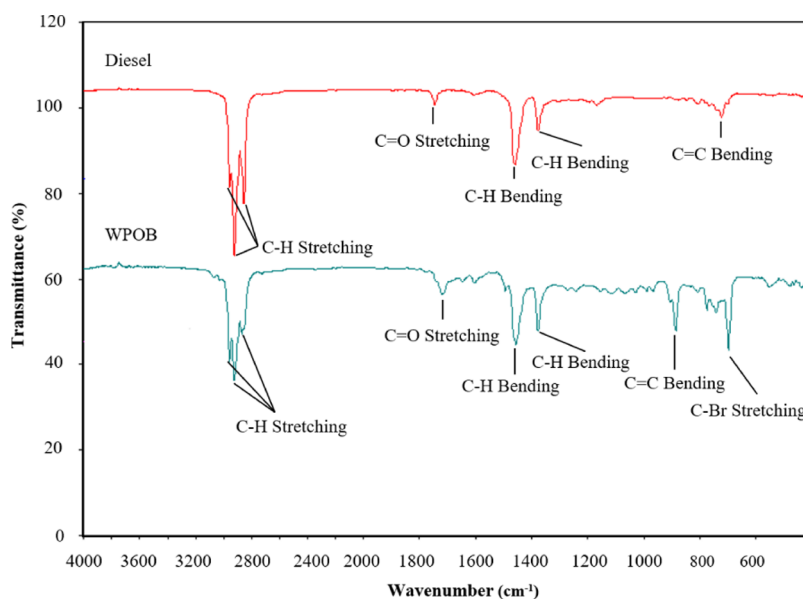
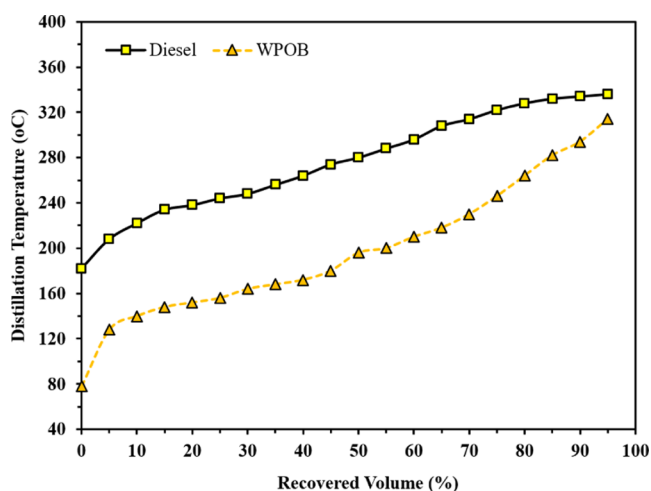
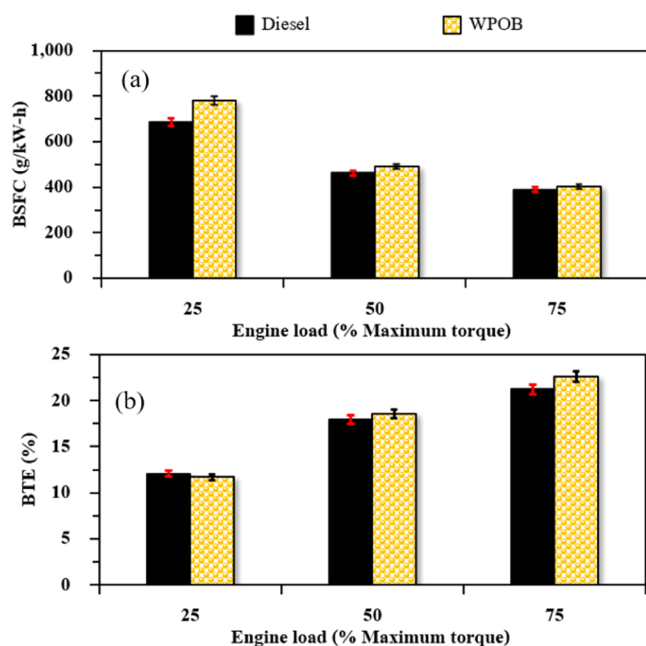


Figure 3. FT-IR spectra analyses of diesel fuel and WPOB.

Table 5. Physical and Chemical Properties of Test Fuels

fuel properties	test method	diesel	WPOB
kinematic viscosity@40 °C (cSt)	ASTM D445	3.37	1.70
specific gravity at 15 °C	ASTM D1298	0.830	0.825
density@15 °C (kg/m ³)	ASTM D1298	829	824
flash point (°C)	ASTM D93	78	28
fire point (°C)	ASTM D93	86	34
gross calorific value (MJ/kg)	ASTM D240	43.48	39.45
cetane index	ASTM D4737	61.09	28.77
lubricity (μm)	ASTM D6079	220	330
distillation temperature (°C)	ASTM D86		
IBP (°C)		188	50
10% recovered (°C)		228	140
50% recovered (°C)		290	196
90% recovered (°C)		342	294
FBP (°C)		348	314

**Figure 4.** Distillation characteristic of WPOB compared to those of diesel fuel.**Figure 5.** Comparison of the engine performance of WPOB as compared to diesel fuel: (a) BSFC and (b) BTE.

of fuel atomization, which directly relates to the quality of air–fuel mixing. However, the very low viscosity of fuel can result in high consumption of fuel.^{25,26} A low flash point and fire point were found with WPOB because of the high content of C₄–C₁₁ (light hydrocarbons) and the low boiling point, which had a worse effect on safe storage and handling.¹⁰ On the other hand, the gross calorific value and the cetane index of WPOB were less than those of diesel fuel. The cetane index of test fuels was calculated by the empirical equation as a function of distillation temperature values of 10, 50, and 90% recovered and of the density or API gravity at 15 °C.²⁷ The difference in properties of test fuels is expected to result in different combustion and emission characteristics, leading to a difference in engine performance.

Meanwhile, the lubricity of WPOB was evaluated using HFRR. It was observed that WPOB possesses poor lubricating properties with respect to diesel fuel, as can be found from the wear scar diameter values of test fuels. This may be due to the lower viscosity of WPOB.^{8,28} The distillation characteristics of test fuels were tested according to the ASTM D86 standard method. The experimental results of the distillation temperature of both fuels show that the lower front-end volatility (10% recovered), mid-boiling point (50% recovered), and back-end volatility (90% recovered) were found with WPOB than with those of diesel fuel. Moreover, WPOB showed a 57% recovered percentage fall within the boiling point temperature range of gasoline (40–200 °C) and a 43% fall within the boiling point temperature range of diesel fuel (200–325 °C) (see Table 5 and Figure 4). This characteristic could be related to the chemical composition of the test fuels and can impact the combustion characteristics of the engine.²⁹ However, the final boiling point of WPOB was within the acceptable maximum limit of the ASTM standard.

Some studies have recently been published on improving the physical and chemical properties of waste plastic oil by various methods such as refining or blending with diesel fuel to make the waste plastic oil suitable to be used as an alternative fuel in diesel engines. The distillation process is one of the methods to improve the fuel characteristics of WPOB using a refinery unit. However, the disadvantages of the distillation process are its high energy usage and increasing cost of fuel production. Therefore, blending with diesel fuel is interesting to improve the fuel characteristics because of its simple method and easy usage along with reducing exhaust gas emissions from IC engines.^{30–32}

3.3. Analysis of Engine Performance. The experimental results were analyzed to determine the engine performance of the diesel engine by running on WPOB compared with diesel fuel operation. Generally, important engine parameters such as specific fuel consumption and thermal efficiency were evaluated based on the engine characteristics in IC engines.

In this study, the brake-specific fuel consumption (BSFC) can be calculated as the mass flow rate of fuel per unit of engine brake power at the engine speed of 1500 rpm. The BSFC of the engine is an important parameter to evaluate the engine performance. The variation of BSFC against engine operating loads for WPOB and diesel fuel is shown in Figure 5a. The experimental results showed that the BSFC of WPOB and diesel fuel decreased with the increase in engine operating load. The BSFC of the test engine in the case of using WPOB was higher than that in the case of using diesel fuel for all engine operating loads, which perhaps resulted from the lower viscosity and gross calorific value of WPOB. More fuel may be required to produce the same engine power output.^{33,34}

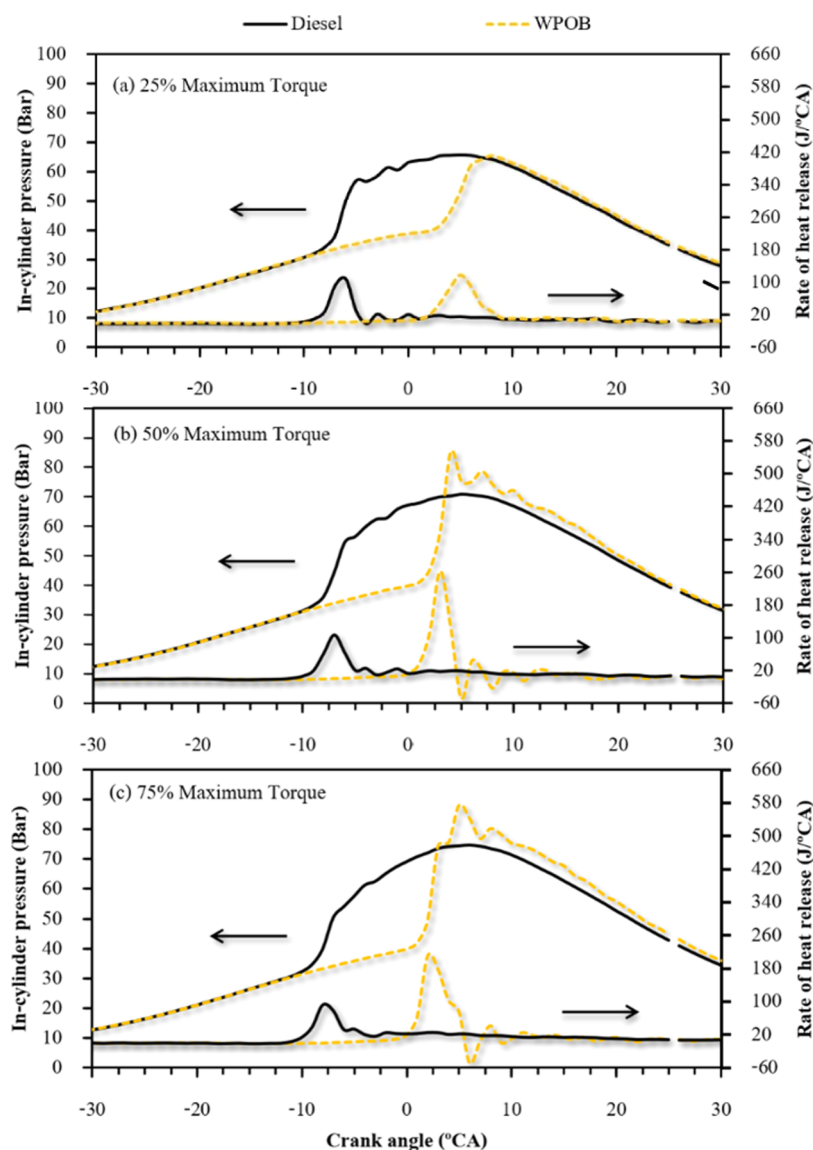


Figure 6. Comparison of combustion characteristics of WPOB as compared to those of diesel fuel at (a) 25% maximum torque, (b) 50% maximum torque, and (c) 75% maximum torque.

Additionally, the brake thermal efficiency (BTE) indicates the ratio of the brake power output established by the fuel energy supplied to the engine. The variation of BTE against engine operating loads for diesel fuel and WPOB is shown in Figure 5b. The BTE increased with the increase in applied engine load significantly with both fuels. This may be attributed to the reduction in heat loss in the combustion chamber as the engine load increases, and also the quantity of injected fuel affects the rise of the cylinder temperature.^{13,35} Comparing the BTEs of the engine, the results show that the BTE of WPOB was lower than that of diesel fuel for low engine load operation. Owing to their higher aromatic content when compared to diesel fuel, more energy may be required for the breaking of aromatic bonds. Another reason that may contribute to the lower BTE of WPOB when compared to diesel fuel is the longer ignition delay period of combustion with WPOB.^{36,37} However, the BTE of WPOB was found to be higher than that of diesel fuel during middle and high engine load operations. This may be due to the better mixing preparation of air and fuel, which resulted in better combustion.³⁸

3.4. Analysis of Combustion Characteristics. In this section, analysis of combustion characteristics of WPOB and diesel fuel was carried out on the diesel engine. The combustion characteristics from fuel combusted within the combustion chamber of the engine are directly affected by fuel properties and engine design parameters. Combustion characteristics of test fuels in this study were investigated based on the cylinder pressure to analyze the combustion process. The cylinder pressure data of 100 cycles were measured and analyzed. The important parameters in the combustion phenomenon of the CI engine are the in-cylinder pressure (ICP) and the rate of heat release (RoHR). RoHR can be derived from energy conservation according to the first law of thermodynamics where products of combustion were assumed to be ideal gases.³⁹ The combustion characteristics obtained under this study are summarized as follows.

The experimental results in Figure 6 show the variation of ICP and RoHR against the crank angle for WPOB as compared to that for diesel fuel at different engine operating loads. It can be observed that the ICP and RoHR increase as the engine

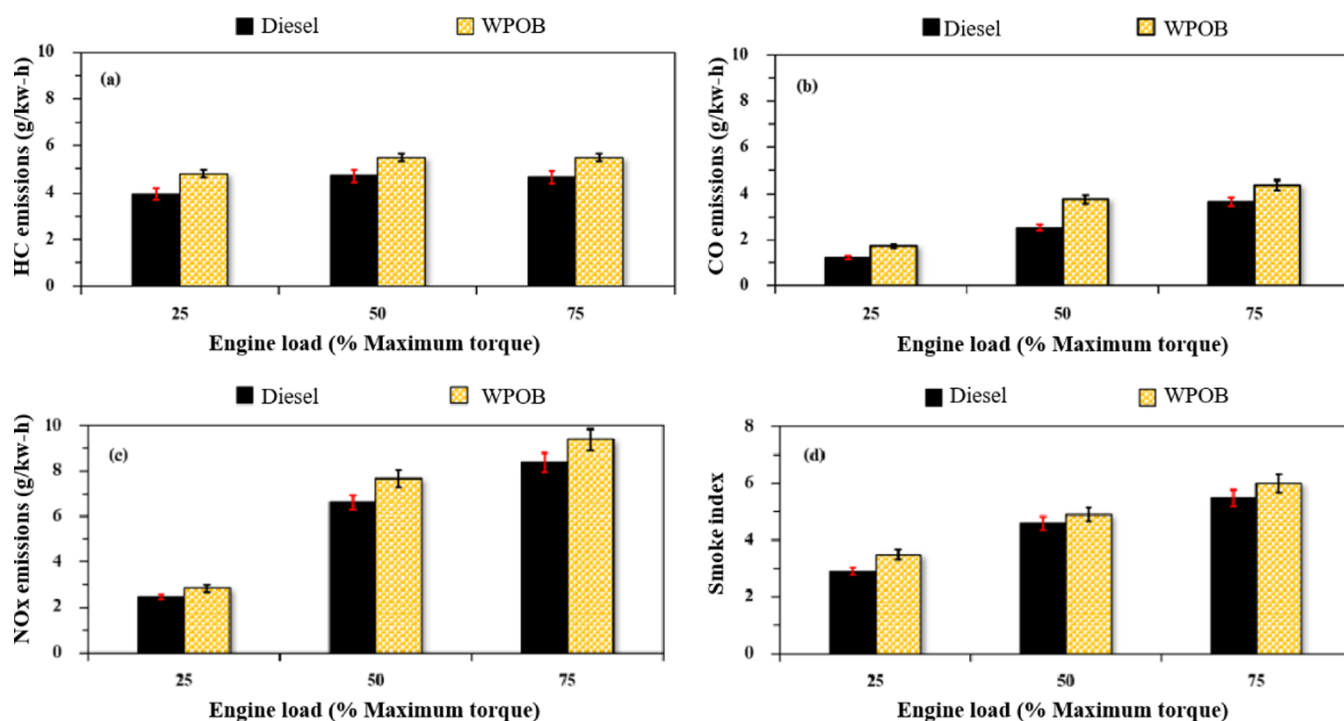


Figure 7. Comparison of exhaust gas emission characteristics of WPOB as compared to those of diesel fuel: (a) HC emissions, (b) CO emissions, (c) NO_x emissions, and (d) smoke index.

Table 6. Difference in PM-Loaded Filter Weight for WPOB and Diesel Fuel

test fuels	weight of filter paper (g)		
	before	after	percentage
diesel	0.0921	0.1211	+31.49
WPOB	0.0905	0.1732	+91.38

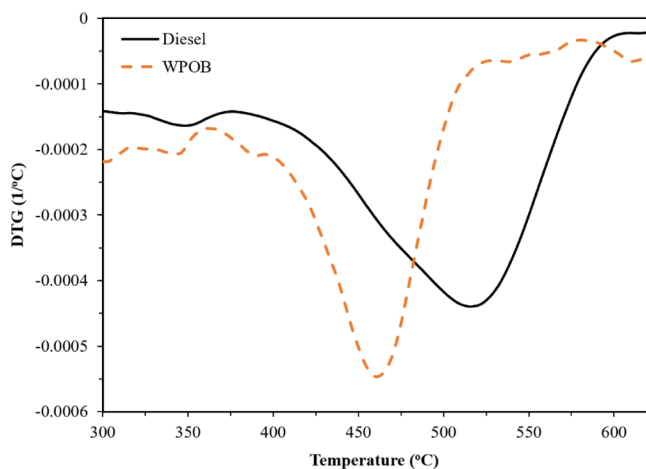


Figure 8. TGA analysis for PM emissions of WPOB and diesel fuel.

operating load increases for both fuels. The reason for increasing ICP and RoHR is due to high amounts of fuel supplied to the engine with an increase in engine operating load. In addition, the pressure in the combustion chamber of the engine depends on the burning rate of the fuel during the premixed burning phase.⁴⁰ Obviously, a longer ignition delay at the start of combustion was obtained with WPOB, resulting in the higher peak of ICP and RoHR compared to that of diesel fuel.⁴¹ Such combustion characteristics of WPOB are not favorable to the ideal

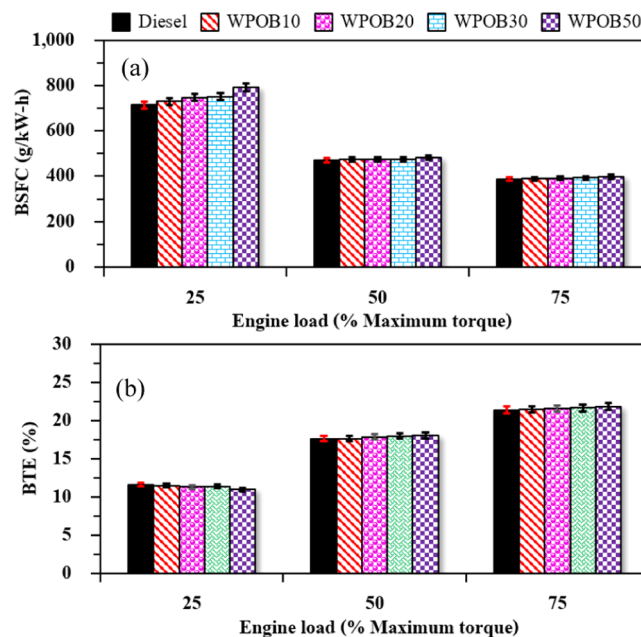


Figure 9. Comparison of engine performances for WPOB blends: (a) BSFC and (b) BTE.

combustion process and can have adverse effects on exhaust gas emissions. The main reason that can justify the long ignition delay at the start of combustion was the lower cetane index of WPOB.⁴²

3.5. Analysis of Emission Characteristics. The total hydrocarbon (HC) emissions of the CI engine are a result of the incomplete combustion caused by the unburned fuel inside the combustion chamber due to overmixing of the fuel and overpenetration of the fuel spray during ignition delay.⁴³ The variations of the HC emissions under various engine operating

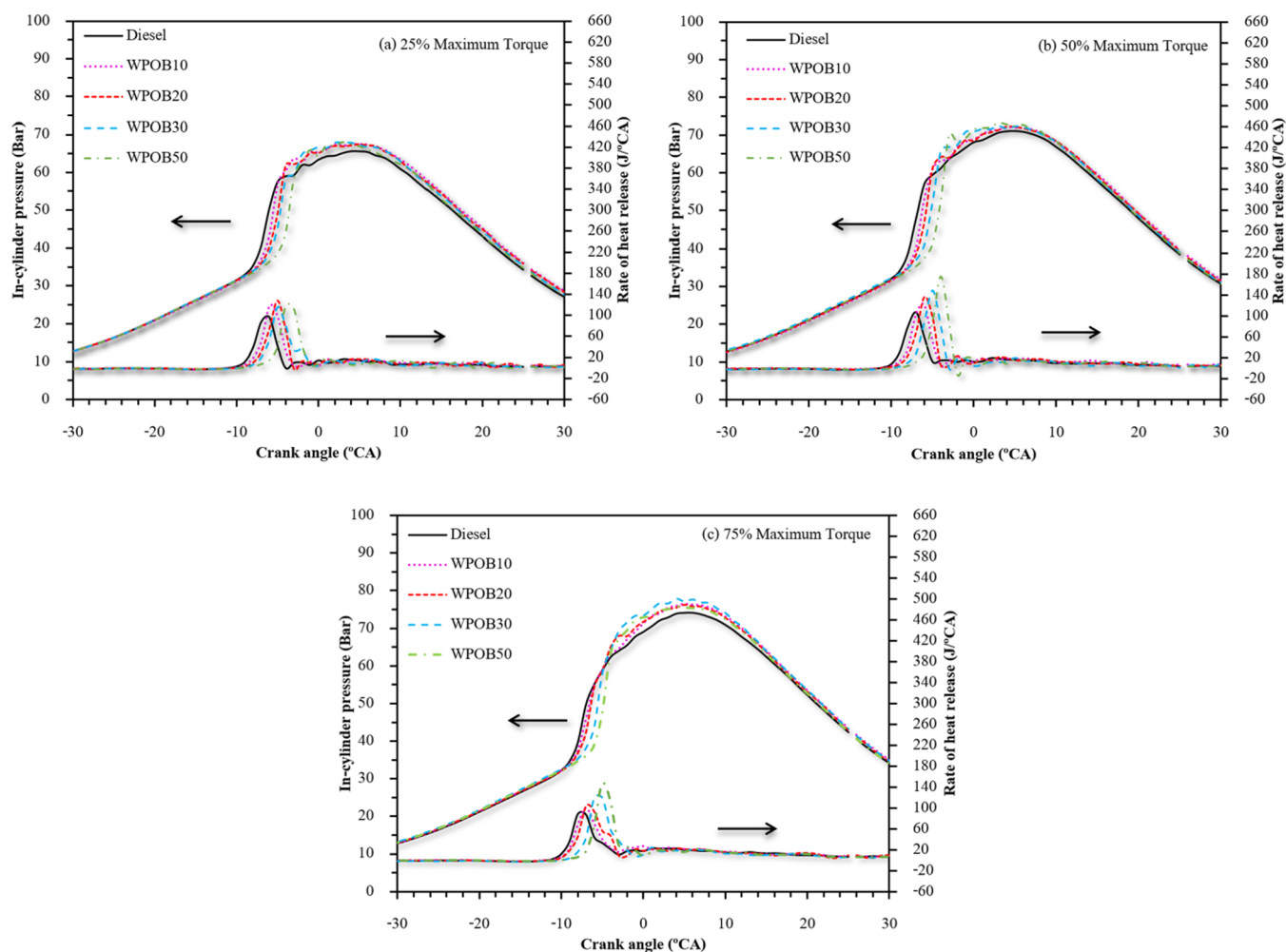


Figure 10. Comparison of combustion characteristics of WPOB blends as compared to those of diesel fuel at (a) 25% maximum torque, (b) 50% maximum torque, and (c) 75% maximum torque.

loads for WPOB and diesel fuel are illustrated in Figure 7a. It can be seen that as the engine operating load increased, HC emissions tended to increase for both fuels. Comparing WPOB and diesel fuel, the HC emissions of WPOB were higher than those of diesel fuel for all engine operating loads. This is mainly due to the longer ignition delay of WPOB, which results in less available time for complete combustion leading to higher HC formation.⁴⁴ However, the oxygen content of the methyl ester present in diesel fuel can participate in better complete combustion.⁴⁵

Carbon monoxide (CO) emissions in the CI engine are formed mainly due to the incomplete combustion of the fuel during the combustion process, which is exacerbated by the deficiency of oxygen, the poor mixture preparation, and the residence time. Usually, the CO emissions from diesel engine combustion are low because the diesel engine is normally operated with a lean air–fuel mixture.^{46,47} Figure 7b represents the variation of the CO emissions under various engine load conditions for diesel fuel and WPOB. It is observed that the CO emissions increase as the engine operating load increases for both fuels. On comparing WPOB and diesel fuel, the CO emissions of WPOB were found to be higher than those of diesel fuel for all engine load operations. This may be due to the lower gross calorific value of WPOB tending to produce less energy during the combustion process, resulting in the higher

possibility of incomplete combustion.⁴⁸ Also, the longer ignition time can justify such higher CO emissions when WPOB was used to operate the engine.

The nitrogen oxide (NO_x) emission in exhaust gas emissions of CI engines is the combination of two components, namely, nitric oxide (NO) and nitrogen dioxide (NO_2).⁴⁹ The variation of NO_x emissions under various engine operating loads for diesel fuel and WPOB is illustrated in Figure 7c. It was observed that NO_x emissions increase as the engine operating load increases for both fuels. A higher in-cylinder pressure and temperature were found as the engine operating load increased. The NO_x formation in diesel engines is mainly dependent on the temperature of combustion inside the cylinder, where a higher in-cylinder temperature was more favorable to form NO_x .^{50,51} The NO_x emissions of WPOB were higher than those of diesel fuel for all engine operating loads. The main reason for the increased NO_x emissions is the higher peak of RoHR during the premixed combustion caused by the longer ignition delay of WPOB, where a higher amount of fuels was prepared before ignition, leading to a stronger combustion and a higher heat release rate.⁵²

The variation of smoke emissions under various engine operating loads for diesel fuel and WPOB is illustrated in Figure 7d. It was observed that smoke emissions increased with the increase of engine operating load for both fuels. On comparing

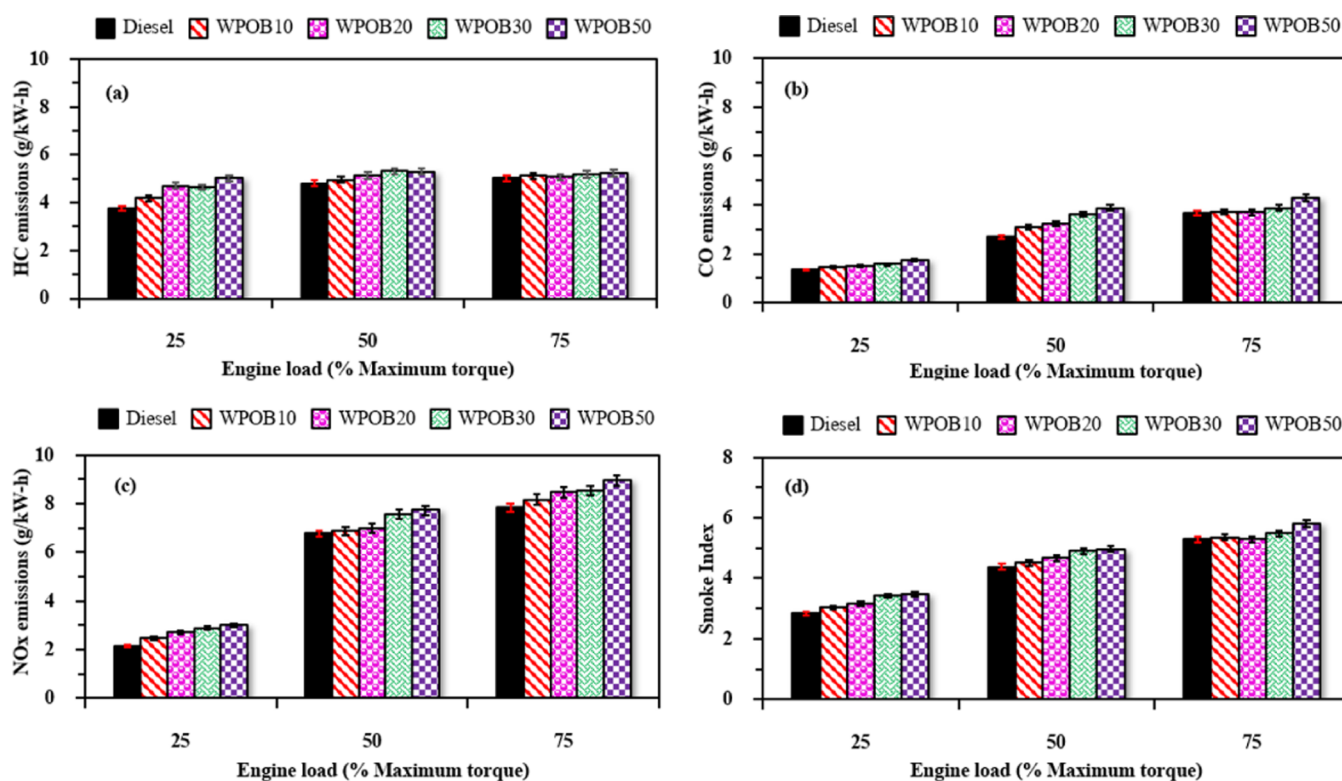


Figure 11. Comparison of exhaust gas emission characteristics for WPOB blends as compared to diesel fuel: (a) HC emissions, (b) CO emissions, (c) NO_x emissions, and (d) smoke index.

WPOB and diesel fuel, the smoke emissions of WPOB were higher than those of diesel fuel for all engine load operations. This is mainly due to the less available time for the combustion process and also the high aromatic content, which contributes to PM formation, resulting in higher smoke emissions obtained with WPOB.⁵

3.6. Analysis of PM Emissions. The difference in the PM-loaded filter weight obtained with test fuels is shown in Table 6. It is clear that the combustion of WPOB produced a higher PM content compared to diesel fuel. This increase in PM emissions is in agreement with the increase in smoke emissions caused by the combustion of WPOB with respect to diesel fuel. In addition, the TGA results in Figure 8 present the percentage of weight loss and its first derivative (DTG) profiles related to the heating program of TGA. It was found that the temperature to reach the maximum rate of soot oxidation (second peak of DTG) was lower with WPOB combustion, which implied that the energy used to oxidize soot was lower and soot was easier to decompose. This is the benefit of using WPOB as an alternative fuel, as was found in the study.

3.7. Possibility of Using WPOB as a Blend Component in Diesel Engines. The significant delay at the start of combustion and the increase in NO_x, HC, CO, and smoke emissions make the direct use of WPOB in diesel engines unsuitable without any engine modification. It is suggested that WPOB can be used as a blend component to reduce the amount of diesel fuel used in diesel engines. To accomplish the objective of the study related to the possibility of using WPOB in diesel engines, an experimental investigation was carried out with four blend ratios of WPOB and diesel fuel, namely, WPOB10, WPOB20, WPOB30, and WPOB50, where the numbers refer to 10, 20, 30, and 50% of the WPOB present in diesel fuel, respectively. Further study on the effect of diesel fuel blended

with WPOB on engine performance, combustion characteristics, and emissions was performed and has been discussed.

3.7.1. Analysis of Engine Performance. The comparison of the engine performance characteristics obtained with the four fuel blends versus diesel fuel for all engine operating loads is shown in Figure 9. From the experimental results obtained, it can be seen that the BSFC increases with an increase in concentration of WPOB in diesel fuel due to the lower heating value of fuel blends compared to that of diesel fuel,¹⁴ whereas the BTE decreased slightly when increasing the concentration of WPOB in diesel fuel at a low engine load operation. However, the BTE tended to increase as the presence of WPOB increased at middle and high engine load operations. No significant change in BSFC and BTE was found when less than 50% WPO was blended with diesel fuel. The presence of 10% WPOB in the fuel blend shows very similar BSFC and BTE compared to diesel fuel.

3.7.2. Analysis of Combustion Characteristics. The experimental results in Figure 10 present the variation of ICP and RoHR with the crank angle degree for fuel blends. It is an important observation that increasing the concentration of WPOB tended to increase the ignition delay period when compared with diesel fuel for all engine operating loads. This is mainly due to the poor ignition of WPOB during the early stage of the combustion process, resulting from the lower cetane index of WPOB.³⁵ The higher percentage of WPOB in the fuel blend tended to increase the peak of the in-cylinder pressure and heat release. The longer ignition with increasing amounts of WPOB in the fuel blend can be used to justify the higher peak.^{12,38} However, the combustion characteristics of WPOB10 were found to be similar to those of diesel fuel in terms of ICP and RoHR.

3.7.3. Analysis of Emission Characteristics. The comparison of the exhaust gas emissions characteristics for fuel blends compared to diesel fuel for all engine operating loads is shown in Figure 11. It can be observed that the exhaust gas emissions of the engine comprising HC, CO, NO_x, and smoke tended to increase on increasing the concentration of WPOB in the diesel fuel. This is mainly due to the longer ignition delay period of WPOB blends along with the less available time for the combustion process. Also, the higher aromatic content present in WPOB can be the reason for the higher smoke and PM emissions compared to diesel fuel.⁵³

4. CONCLUSIONS

In conclusion, an experimental investigation was carried out to evaluate the effect of pyrolytic plastic oil derived from waste PET bottle (WPOB) on engine performances, combustion characteristics, exhaust gas emissions, and soot oxidation temperature. The summary of this study can be discussed as follows.

- The chemical compositions of WPOB and diesel fuel were characterized by GC–MS. It was found that the main hydrocarbons present in WPOB were in a group of C₆–C₁₂ with the major chemical compounds of benzene, ethylbenzene, heptane, toluene, and xylene, while diesel fuel possessed a high content of C₁₃–C₁₈. In addition, similar FT-IR spectra were seen for the diesel fuel and WPOB. However, WPOB shows the presence of mostly aromatic compounds. The fuel property characterization, including a lower kinematic viscosity, specific gravity, density, flash point, fire point, gross calorific value, cetane index, distillation temperature, and lubricity, of WPOB was compared to that of diesel fuel. The API gravity of WPOB was higher when compared to that of diesel fuel.
- The engine characteristics show that using WPOB in the diesel engine tends to increase the BSFC and BTE. Moreover, the combustion characteristics of WPOB were retarded during the start of combustion with respect to those in diesel fuel, which result in an increase in HC, CO, NO_x, and smoke emissions. However, the TGA results show that the temperature to reach the maximum rate of soot oxidation was lower with WPOB combustion. This result shows that the direct use of WPOB in diesel engines is not recommended. Therefore, it is suggested that WPOB can be used as a blend component to reduce the amount of diesel fuel used in diesel engines.
- The results of this study further demonstrate that the maximum WPOB that should be present in the diesel fuel to avoid the long ignition delay during the start of combustion and the increase in HC, CO, and smoke emissions is 20% by volume to keep the engine characteristics and emissions similar to those in diesel fuel, especially when the engine was operated at middle and high loads.

■ AUTHOR INFORMATION

Corresponding Author

Jiraphon Srisertpol – School of Mechanical Engineering, Institute of Engineering, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand; orcid.org/0000-0002-4341-3708; Email: jiraphon@sut.ac.th

Authors

- Somkiat Maithomklang** – School of Mechanical Engineering, Institute of Engineering, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand
- Khatha Wathakit** – School of Agricultural and Food Engineering, Institute of Engineering, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand
- Ekarong Sukjit** – School of Mechanical Engineering, Institute of Engineering, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand; orcid.org/0000-0003-4641-2580
- Boonlue Sawatmongkhon** – College of Industrial Technology, King Mongkut's University of Technology North Bangkok, Bangkok 10800, Thailand; Research Centre for Combustion and Alternative Energy (CTAE), Science and Technology Research Institute, King Mongkut's University of Technology North Bangkok, Bangkok 10800, Thailand; orcid.org/0000-0001-8972-4387

Complete contact information is available at:

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Notes

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■ NOMENCLATURE

- ASTM American Society for Testing and Materials
 BSFC brake-specific fuel consumption
 BTE brake thermal efficiency
 CO carbon monoxide
 DI direct injection
 DTG derivative thermogravimetry
 FT-IR Fourier transform infrared spectroscopy
 GC–MS gas chromatography–mass spectrometry
 HC hydrocarbon
 HFRR high-frequency reciprocating rig
 ICP in-cylinder pressure
 ICE internal combustion engines
 MW molecular weight
 NO nitric oxide
 NO₂ nitrogen dioxide
 NO_x nitrogen oxides
 PET poly(ethylene terephthalate)
 PM particulate matter
 RoHR rate of heat release
 TGA thermogravimetry analysis
 WPOB waste plastic oil bottle
 WPO waste plastic oil

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