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Article

The Effect of Oxygenated Turpentine Oil Additive in Diesel Fuel on the Performance and Emission Characteristics in One-Cylinder DI Engines

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Abstract: A study on the application of oxygenated turpentine oil as a bio-additive in diesel fuel was conducted. The purpose of this research was to investigate the effect of oxygenated turpentine oil additive in diesel fuel on the performance and emission characteristics in diesel engines. Oxygenated turpentine oil is obtained from the oxidation process of turpentine oil. In this experimental study, the influences of oxygenated turpentine oil-diesel blended fuel OT0.2 (0.2% vol oxygenated turpentine oil and 99.8% vol diesel) were compared with pure diesel on engine performance, and emission characteristics were examined in a one-cylinder four-stroke CI engine. The test was performed at two engine loads (25% and 50%) and seven engine speeds (from 1200–2400 rpm with intervals of 200 rpm). The physiochemical characteristics of test fuels were acquired. The engine indicated power, indicated torque, fuel flow rate, and emissions (carbon dioxide, CO_2; carbon monoxide, CO; and nitrogen oxide, NO_X) were examined. The results revealed that the engine power shows slight increments of 0.7–1.1%, whereas the engine torque slightly decreased with oxygenated turpentine usage compared to pure diesel in most conditions. Furthermore, a reduction in NO_X emission decreased by about 0.3–66% with the addition of oxygenated turpentine in diesel compared to diesel. However, usage of OT0.2 decreased fuel flow rate in most speeds at low load but gave a similar value to diesel at 50% load. CO emissions slightly increased with an average of 1.2% compared to diesel while CO_2 emissions increased up to 37.5% than diesel. The high-water content, low cetane number, and low heating value of oxygenated turpentine oil were the reasons for the inverse effect found in the engine performances.

Keywords: bio-additive; oxygenated turpentine oil; diesel fuel; diesel engine performance; emission

1. Introduction

Diesel fuel is produced from the distillation process of petroleum and is used to fuel diesel engines. Diesel engine usage has become more popular today ever since it was founded in 1983 by Rudolf Diesel. The popularity of diesel engines comes from the advantage of having a low-cost of fuel compared to gasoline engines. There is a wide use of diesel engines from transportation to industrial applications [1–4]. As a result, the amount of harmful gas emissions emitted from diesel fuel combustion such as CO, NO_X, and hydrocarbon (HC) will be increased as well [5–8]. Consequently, this has led to adverse impacts on human health and on the environment. For this reason, a lot of studies have been conducted to minimize harmful gases emitted from diesel engines [9–11].

Mixing diesel fuel with additives is one of the many attempts to reduce emissions from diesel combustion, as well as a way to optimize fuel consumption of the engine. There are many compounds used as diesel fuel additives such as organometals, nitrates, oxygenates (compounds rich with oxygen), and natural matters (bioactive) [12–15]. Organometals and nitrates have been known to increase the burning efficiency of diesel fuel. However, it is also discovered that those additives may result in additional emissions of NO_X that is harmful to humans [16–18]. On the other hand, oxygenates and bio-additives are known to be more environmentally friendly. Nayyar et al. [19] in their recent work stated that the addition of compounds rich in oxygen (oxygenates) into diesel fuel could reduce smoke and NO_X production by 61.85% and 8.07%, respectively. This finding was also supported by other research [20–23], which explained how soot reduction is linearly related to the increasing oxygen mass fraction in the fuel. Other researchers who used oxygenated additives reported enhancement in its application [24–27].

Turpentine oil is often referred to as spirits of turpentine in the form of volatile liquid, derived from the distillation of tree sap species belonging to the pine genus. It is colorless (liquid), has a distinctive smell, and is flammable [28–30]. In general, the physical and chemical properties of boiling turpentine oil is 149–180 °C, insoluble in water, density 0.9, flash point 30–46, auto ignition temperature 220–225 °C (International Program on Chemical Safety and the European Commission, 2002) [31–34]. It contains monoterpenes with C 10 carbon atoms. Turpentine oil is generally composed of a mixture of unsaturated isomers, bicyclic hydrocarbons namely α-pinene, β-pinene, and δ-carene as presented in Figure 1 [28].

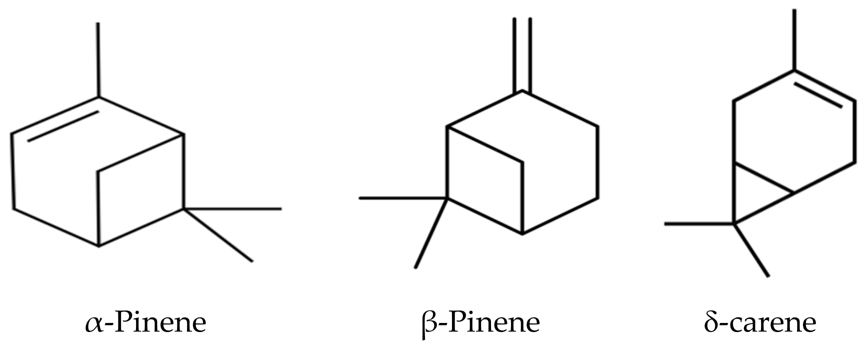


Figure 1. Chemical structure of the main component of turpentine oil.

From the work of Polonowski et al. [35], it is reported that diesel fuel with 5% of pure turpentine oil could reduce smoke production and reduce fuel consumption. This was in line with Butkus' finding that 5% of oxidized turpentine oil was the best diesel fuel additive [36–38]. Furthermore, Kadarohman et al. [39] found that terpene compounds contained in clove oil (0.2%) were largely contributed to make a better mixture between bio-additive and diesel fuel, which lead to rapid combustion and shorter ignition delay in combustion of diesel engines. This discovery is interesting for further investigation on the influence of terpene compounds addition in diesel fuel [40–42].

The four atom C rings on α-pinene and β-pinene have high spatial strain that are reactive. The presence of a double bond causes α-pinene to easily undergo an oxidation reaction when there is air contact, then forms a hydroperoxyl compound which has intermediate molecules that are reactive [43]. The cyclic structure in turpentine oil will effectively disrupt the Van der Waals interaction between the carbon chains of diesel fuel, consequently leading to the diesel oil molecules becoming easier to evaporate, hence accelerating the combustion process [39,44]. The reactive nature of turpentine oil constituents is also expected to accelerate the combustion of diesel fuel. Song et al. [45] suggested that the addition of oxygen enriched additives into diesel fuel has a significant role to increase the cetane number of the fuel. Choi and Reitz [46] mentioned that oxygen atoms in fuel play a major role in oxidizing soot and CO gas.

For this reason, efforts to speed up and to refine the combustion process of diesel fuel can be carried out by enriching the levels of oxygen atoms contained in turpentine oil through the oxidation of the double bonds formed in the compound. In this paper, the effects of additive oxygenated turpentine oil-diesel (0.2% vol and 99.8% vol) on the performance and emission in one-cylinder diesel engines were tested. The experiment was performed at different engine speeds and two engine loads (25% and 50%). The physiochemical characteristics of test fuels were determined. Moreover, the effects of tested fuels upon indicated power, indicated torque, flue flow rate, and emissions characteristics were systematically observed.

2. Materials and Methods

2.1. Materials

In this study, the diesel used was pure diesel Euro2M from Malaysia. Turpentine oil and oxygen gas were from Brataco and Sangkuriang companies, Indonesia. Turpentine oil was oxygenated via the oxidation process. It was carried out by reflux method using a cylindrical column reactor with length and diameter dimensions of 30 cm and 2 cm, respectively. The 15 mL turpentine oil was aerated by oxygen gas with flow rate of 3 L/min and heated by an electrical wire heater at 90–100 °C for 3 h. The oxidation procedure was conducted at Life Science Laboratory, Department of Chemistry, Indonesia University of Education, Bandung Indonesia. Oxygenated turpentine oil as a bio-additive was dissolved in diesel fuel at a volume percent level of 0.2% (note as OT0.2) by a manual direct blending method using a mechanical stirrer IKA RW20 with blending speed 700 rpm for 15 min at room temperature. The characterizations of diesel, turpentine oil, and oxygenated turpentine oil were done by gas chromatography—mass spectrometry GC-MS QP5050A. Diesel fuel and OT0.2 were examined on one-cylinder DI engines in order to obtain their performance and emission.

2.2. Experiment Setup

The test engine was a YANMAR TF120M one-cylinder DI diesel engine with a 17.7 compression ratio. The specifications of the engine and schematic diagram of the set up for this test are shown in Table 1 and Figure 2, respectively. The data were recorded by data acquisition system TFX Engineering, which consisted of in-cylinder pressure and crank angle sensors. Furthermore, exhaust gas temperature and ambient temperature were measured using K-type thermocouples, that were recorded using a TC-08 thermocouple data logger by Pico Technology. The thermocouple was installed at the exhaust manifold. The emissions were measured using KANE Auto 4-1 series exhaust gas analysers. The experiment was conducted with seven speeds from 1200 to 2400 rpm with intervals of 200 rpm and two engine loads at 25% and 50%. The test fuels used were diesel as base line and oxygenated turpentine oil-diesel (0.2% vol and 99.8% vol). The data were recorded under steady state conditions. The engine power, engine torque, the fuel flow rate, and the emissions (CO, CO_2, and NO_x) were measured. The experiment was conducted at Universiti Malaysia Pahang (UMP), Kuantan, Malaysia.

Table 1. Engine Specifications.

Description	Specification
Engine model	YANMAR TF120M
Engine year	2016
Engine type	Horizontal, 4-cycle, 4 stroke, diesel engine
Number of cylinders	1
Continuous power output (kW)	7.82 kW at 2400 rpm
Rated power output (kW)	8.94 kW at 2400 rpm
Bore x Stroke (mm)	92 × 96
Displacement (L)	0.638
Injection timing	17° BTDC

Table 1. *Cont.*

Description	Specification
Compression ratio	17.7
Combustion system	Direct injection
Aspiration	Natural aspiration
Cooling system	Water-cooled
Starting system	Manual (Hand) Starting

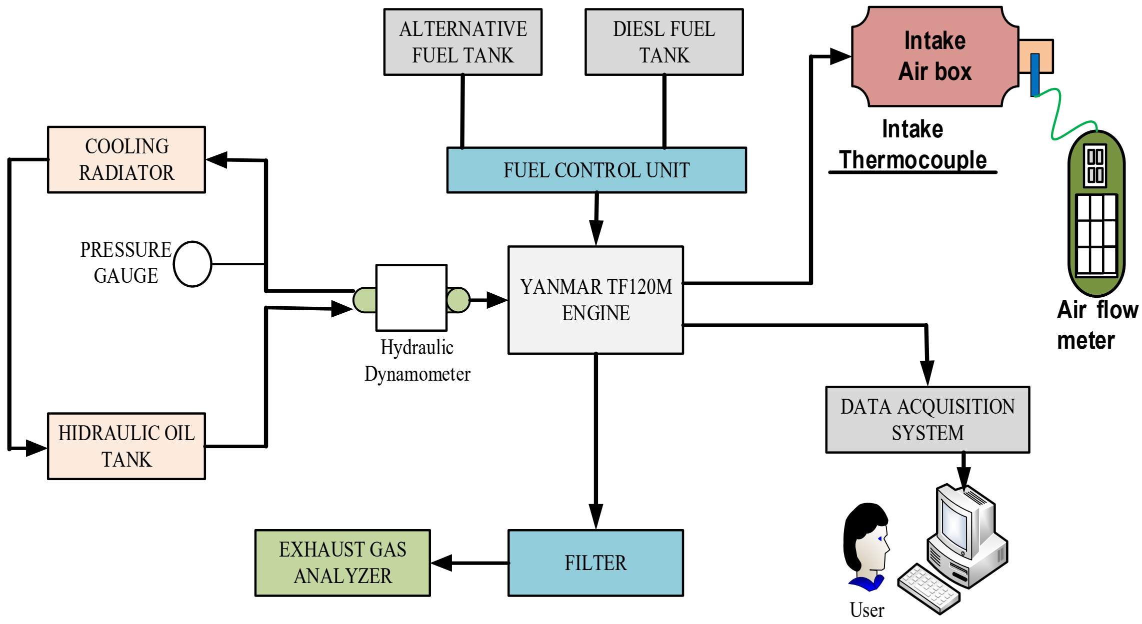


Figure 2. Schematic diagram of diesel engine test set up.

3. Results and Discussion

3.1. Physiochemical Properties

The performed research on physical properties showed that the bio-additive fuel blends were in full compliance with the standard of American Society for Testing and Materials, ASTM D975 specifications for diesel fuel. The physical properties of diesel and OT0.2 were presented in Table 2.

Table 2. Physical properties of test fuels.

Parameters	Diesel Fuel	OT0.2	ASTM D975 Limit	
			Min	Max
Specific Gravity at 25 °C (g/mL)	0.8452	0.8549	-	-
Specific Gravity at 15.55 °C (g/mL)	0.8522	-	0.848	0.87
API Gravity	34.5408	-	-	-
Anilin point (°F)	156.2	159.2	129.6	-
Index Diesel	53.9527	51.3883	-	-
Viscosities (cSt)	3.7215	4.4625	1.3	4.5
Flash Point (°C)	61.89	-	60	80

The diesel, turpentine, and oxygenated enriched turpentine used in this experiment were characterized by GC-MS. Figure 3 shows the chromatogram of diesel fuel, turpentine, and oxygenated turpentine that provides the information of its chemical components and composition. In particular, diesel fuel consisted of saturated hydrocarbons such as normal paraffins, is paraffins, and cycloparaffins. The main components of diesel fuel are hexadecane (n-cetane), pristane (2,6,10,14-tetramethylpentadecane), and is paraffins

(Figure 3a), in line with previous studies [47]. The chemical constituents of diesel fuel are listed in Table 3.

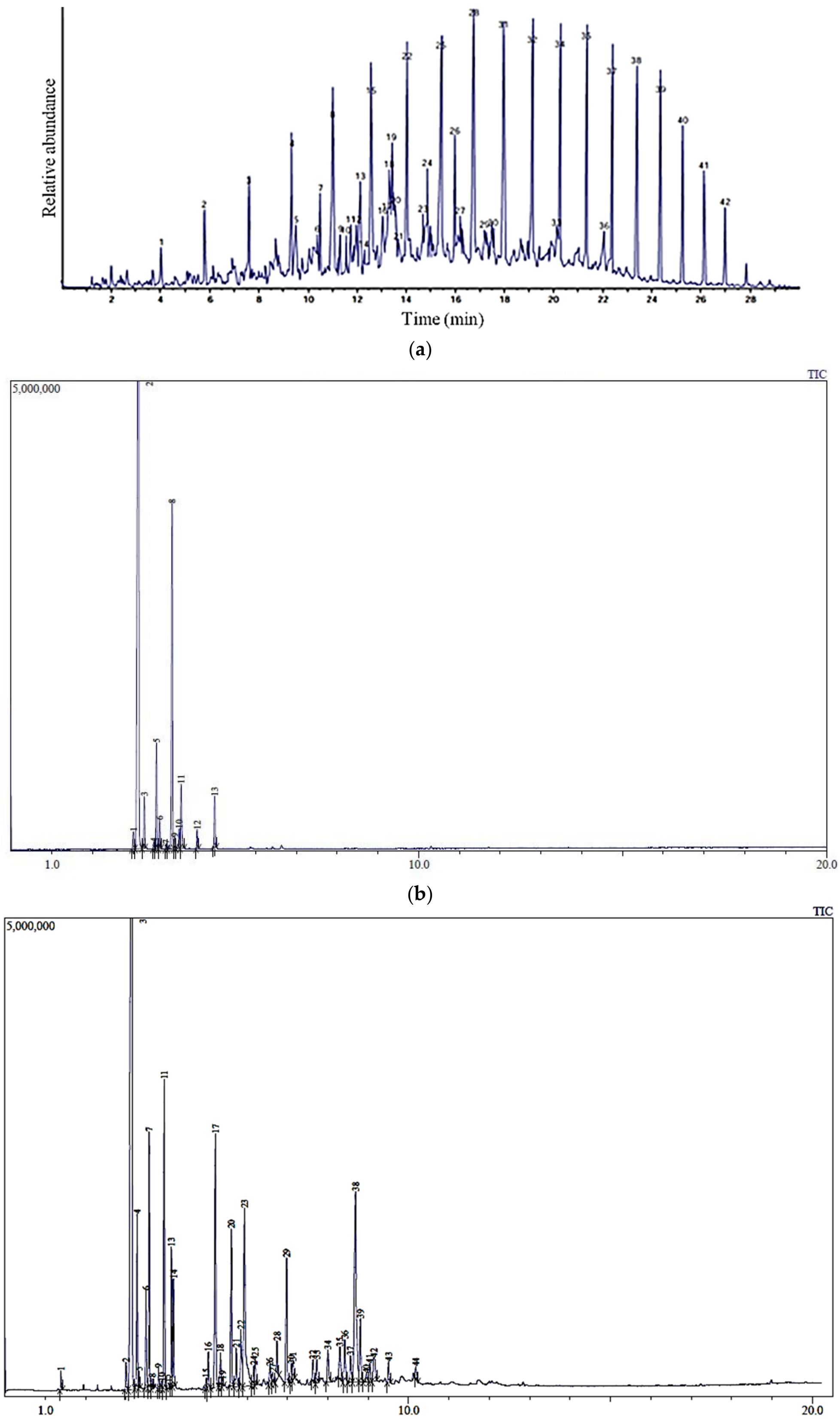
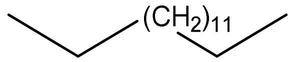
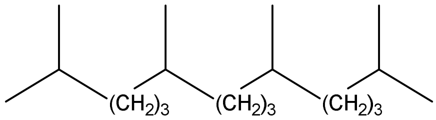
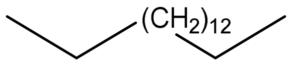
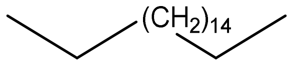
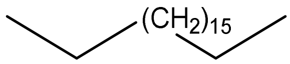
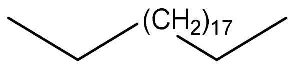
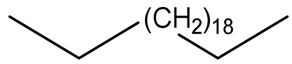
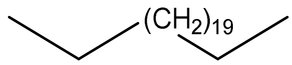


Figure 3. Chromatogram of diesel fuel (**a**), turpentine (**b**), and oxygenated turpentine (**c**).

Table 3. Chemical constituents of diesel fuel.

Peak No	Molecular Formula	Name	Retention Time (Min)	Conc. (%)	Structure
22	$C_{15}H_{32}$	Pentadecane	14.050	5.27	
26	$C_{19}H_{40}$	2,6,10,14-tetramethylpentadecane (pristane)	15.993	2.44	
28	$C_{16}H_{34}$	Hexadecane (n-cetane)	16.769	10.67	
31	$C_{18}H_{38}$	n-octadecane	17.980	7.47	
32	$C_{19}H_{40}$	n-nonadecane	19.151	5.37	
34	$C_{21}H_{44}$	n-heneicosane	20.284	4.84	
35	$C_{22}H_{46}$	n-docosane	21.365	4.81	
37	$C_{23}H_{48}$	n-tricosane	22.404	4.07	

On the other hand, turpentine contains at least 12 compounds as shown in Figure 3b, that are predominantly composed of α-pinene (61.61%), δ-carene (19.70%), β-pinene (4.8%), limonene (3.58%), and camphene (2.25%), with based mass fragment at retention times of 3.127, 3.950, 3.568, 4.712 and 3.267 min, respectively. These results align with previous studies [48]. All chemical compounds of turpentine including its structure and composition is listed in Table 4.

Interestingly, oxidation treatment led to remarkable modifications of turpentine in term of chemical constituents and composition. Figure 3c demonstrates the chemical constituents of oxygenated turpentine where at least 44 compounds were detected by GCMS. In particular, the oxidation process of turpentine yields new compounds with various composition. After oxidation, the composition of major constituents of turpentine experienced a significant reduction, i.e., α-pinene (32.68%), δ-carene (5.77%), β-pinene (4.44%), and limonene (1.93%). This presents new oxygenated compounds with significant composition such as α-pinene-oxide, patchcoulane, trans-verbenol, verbenone, and α-champholene aldehyde at retention times of 5.213, 8.684, 5.932, 6.974, and 5.604, respectively. Details of chemical constituents of oxygenated turpentine are summarized in Table 5. Additionally, the mass fragment of major chemical components of oxygenated turpentine is shown in Figure 4. The oxygenated products contain more oxygen related functional groups, i.e., hydroxyl (-OH), aldehyde (-HC=O), and ketone (-C=O). These results indicated the effectiveness of selected oxidation procedures of turpentine where the predominant oxygenated compounds came from the oxidation of α-pinene and δ-carene as the most major constituents of turpentine.

Table 4. Major chemical constituents of turpentine.

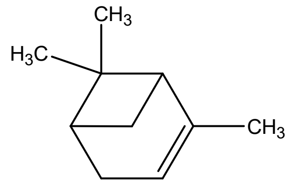
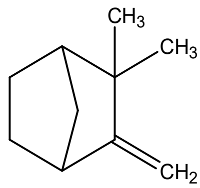
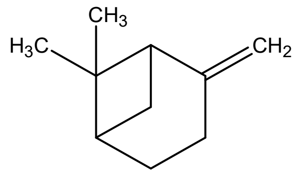
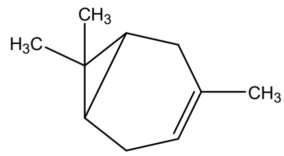
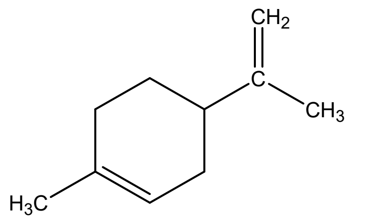
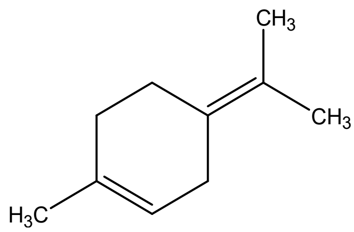
Peak No	Molecular Formula	Name	Retention Time (Min)	Conc. (%)	Structure
2	$C_{10}H_{16}$	Alpha-pinene	3.127	61.81	
3	$C_{10}H_{16}$	Camphene	3.267	2.25	
5	$C_{10}H_{16}$	Beta-pinene	3.568	4.80	
8	$C_{10}H_{16}$	Delta 3 Carene	3.950	19.70	
11	$C_{10}H_{16}$	dl-Limonene	4.172	3.58	
13	$C_{10}H_{16}$	Alpha-terpinolene	4.993	2.49	

Table 5. Major chemical constituents of oxygenated turpentine.

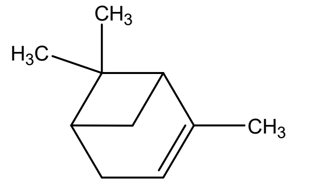
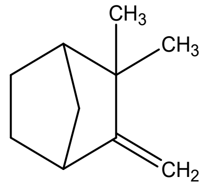
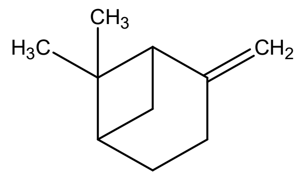
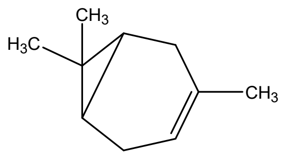
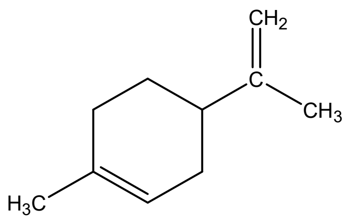
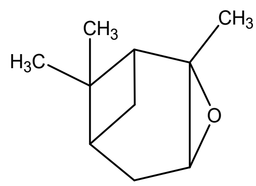
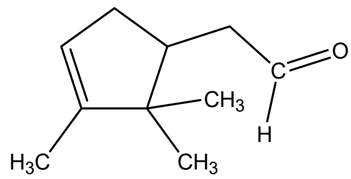
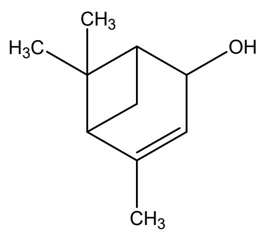
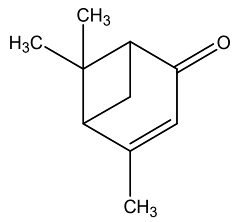
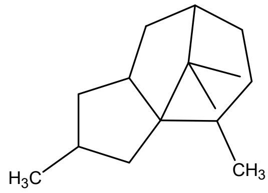
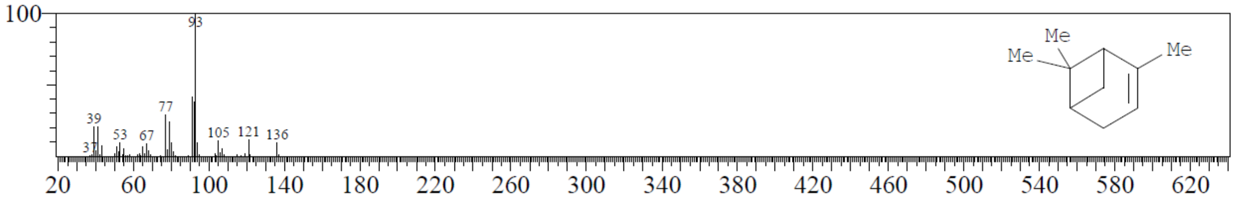
Peak No	Molecular Formula	Name	Retention Time (Min)	Conc. (%)	Structure
3	$C_{10}H_{16}$	Alpha-pinene	3.143	32.68	
4	$C_{10}H_{16}$	Camphene	3.272	2.94	
7	$C_{10}H_{16}$	Beta-pinene	3.571	4.44	
11	$C_{10}H_{16}$	Delta 3 Carene	3.944	5.77	
14	$C_{10}H_{16}$	dl-Limonene	4.173	1.93	
17	$C_{10}H_{16}O$	Alpha-pinene oxide	5.213	6.15	
20	$C_{10}H_{16}O$	Alpha-campholene aldehyde	5.604	3.59	
23	$C_{10}H_{16}O$	Trans-verbenol	5.932	6.66	

Table 5. *Cont.*

Peak No	Molecular Formula	Name	Retention Time (Min)	Conc. (%)	Structure
29	$C_{10}H_{14}O$	Verbenone	6.974	3.11	
38	$C_{15}H_{26}$	Patchoulane	8.684	8.29	

3.2. Engine Performance

Figures 5 and 6 show comparison results of indicated power and indicated torque at various engine speeds and loads, respectively. The power and torque depended on the fuel supplied and engine operating conditions. In this study, at the maximum engine speed of 2400 rpm, the indicated power of the engine slightly increased with the addition of an oxygenated additive compared to diesel fuel. The average increment when an additive was introduced into diesel was 0.7% to 1.1%. The higher oxygen content in oxygenated turpentine improved the in-cylinder combustion reaction process, hence producing higher power than diesel [33,49,50]. Another reason is due to higher fuel mass flow used for additive fuel. The increments were supported by a few studies that used oxygenated additives in the fuel [51–53]. On the other hand, the torque profile for low and high loads of oxygenated turpentine was found to be lower than diesel. The decrement is due to the increase in mass and flow resistance and the decrease in volumetric efficiency [33,54].



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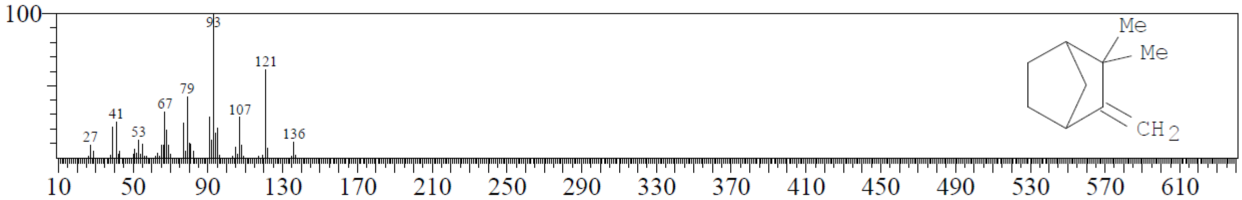
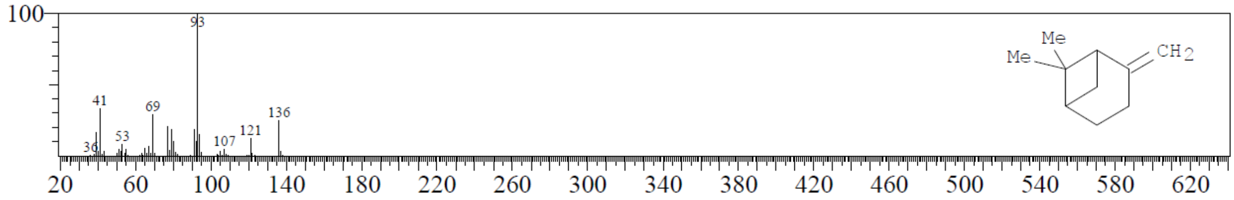


(**b**)

Figure 4. *Cont.*



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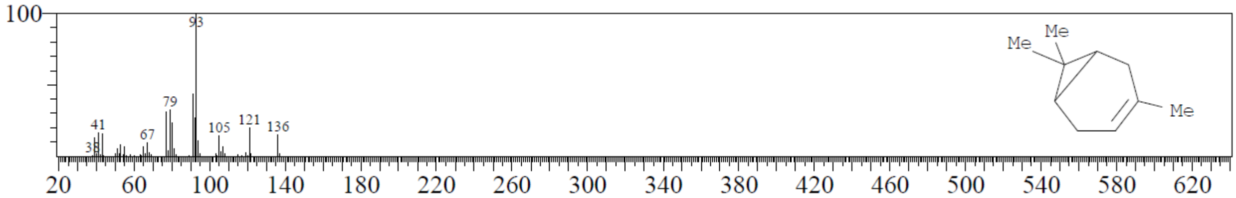

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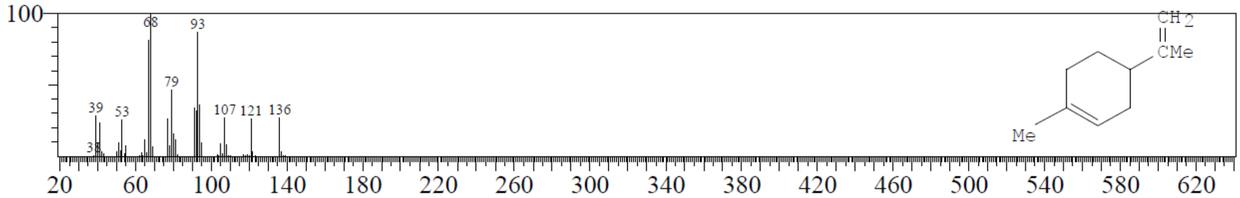
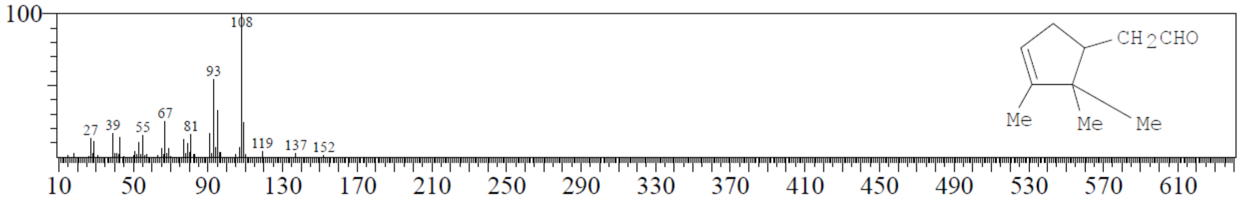
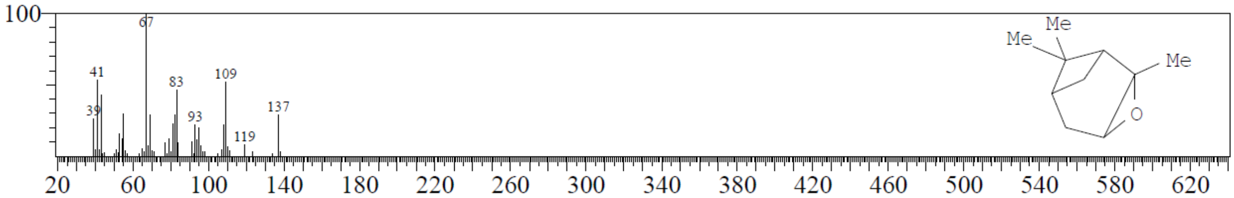


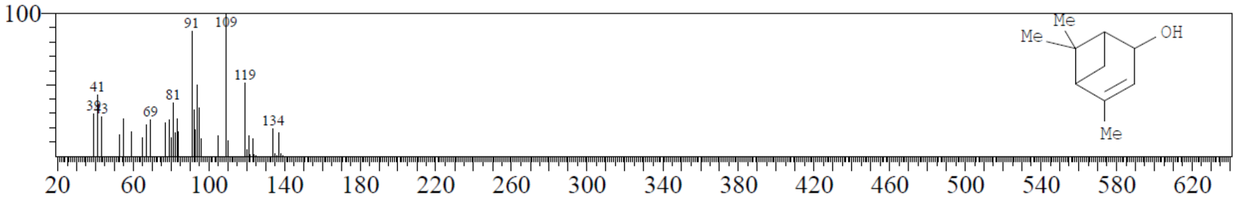
(**e**)



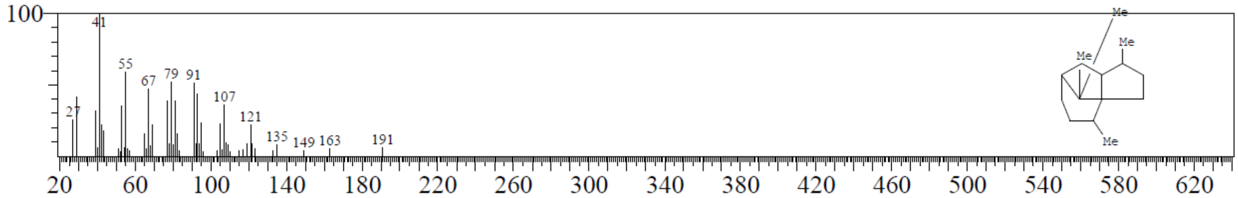
(**f**)



(**g**)



(**h**)



(**i**)

Figure 4. Mass fragments of α-pinene (**a**), camphene (**b**), β-pinene (**c**), δ-carene (**d**), limonene (**e**), α-champholene aldehyde (**f**), α-pinene oxide (**g**), trans-verbenol (**h**), and Patchoulane (**i**) for oxygenated turpentine.

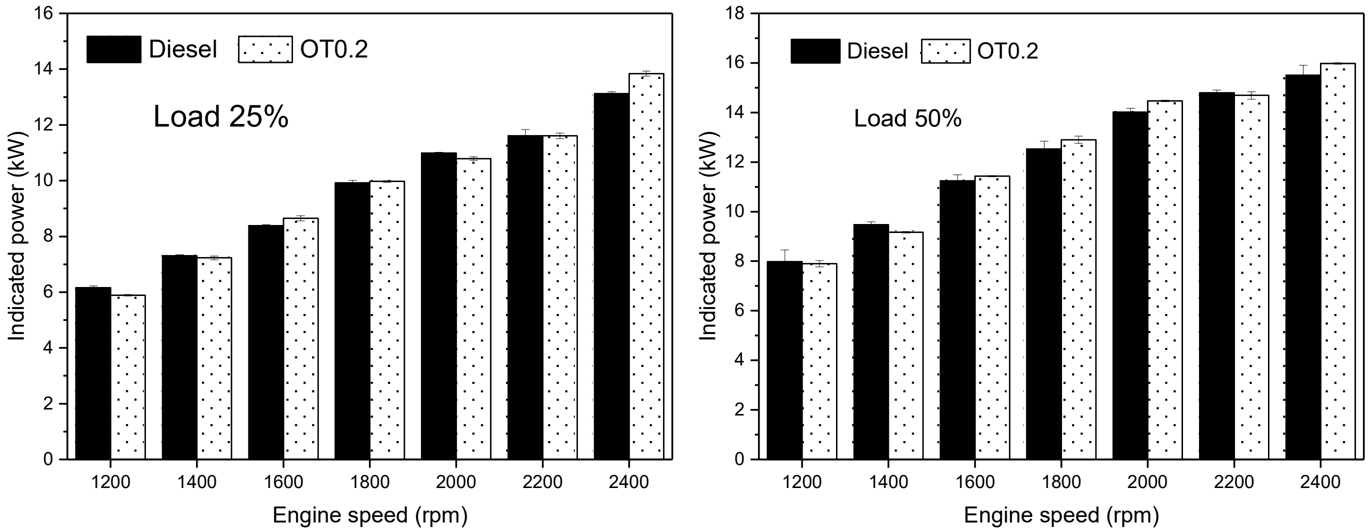


Figure 5. Indicated power at various engine speeds.

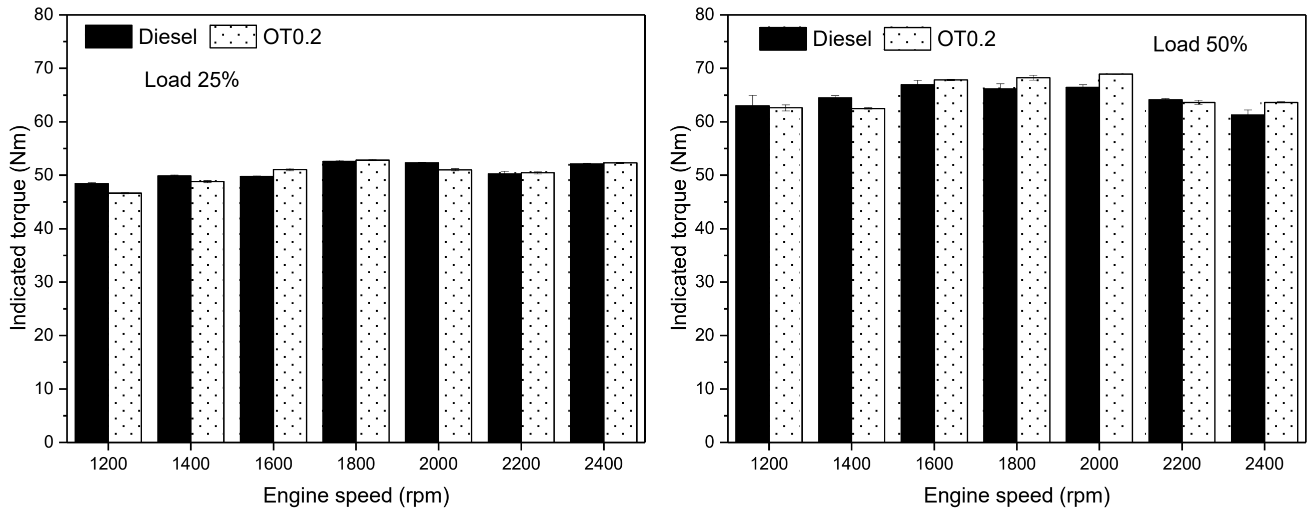


Figure 6. Indicated torque at various engine speeds.

Figure 7 presents the variations of fuel flow rates at different speeds and loads for diesel and oxygenated turpentine oil-diesel fuel. Mostly, the flow rate increases with the increment of engine speed and load. At low load cases, at most engine speeds, there are decrement of fuel flow rate of additive fuel compared to diesel. The enhancement rate of fuel flow while using an additive are between 5 to 9.09% compared to diesel. However, at 50% load, oxygenated turpentine oil-diesel fuel shows a slight increment of fuel flow rates with diesel at most engine speeds. The percentage of increment of fuel flow rate while using an additive at 50% load are in the range of 0.42 to 10.67%, compared to diesel. It is due to the lower heating value of oxygenated turpentine oil—diesel that requires higher fuel consumption. In contrast, at medium load with high speeds, 2200 and 2400 rpm, fuel flow rate of oxygenated turpentine oil-diesel fuel shows reduction up to 4.6% compared to diesel.

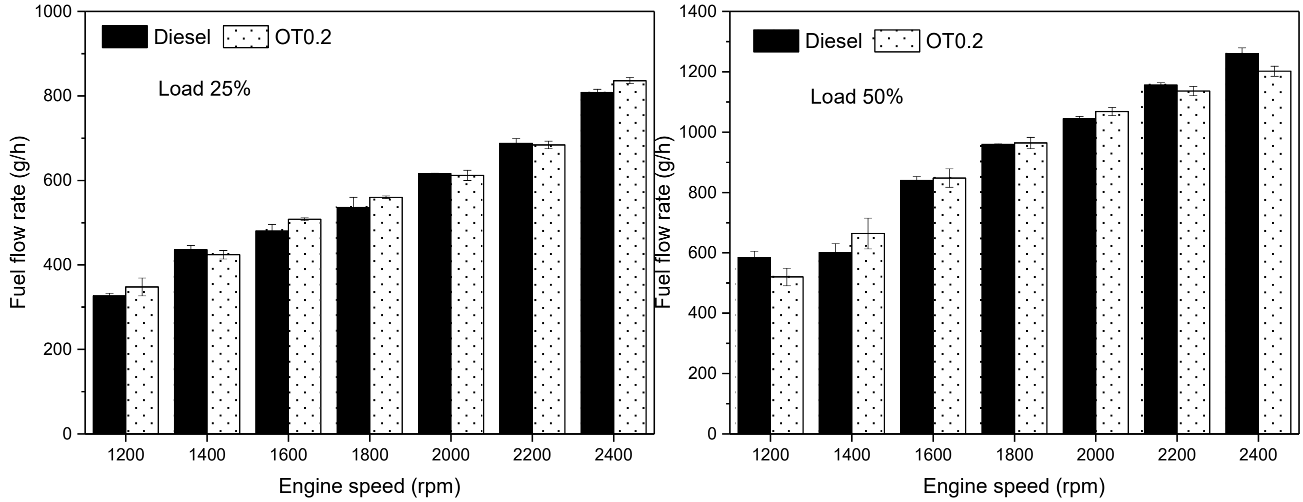


Figure 7. Fuel flow rate at various engine speeds.

3.3. Gas Emissions

In general, carbon monoxide emission shows a decline pattern when oxygenated additives are introduced into diesel fuel [55–57]. Reduction in CO occurs due to oxygenated characteristics of fuel and well-flammability properties of the oxygenated additive. Furthermore, the higher latent heat of evaporation in oxygenated-based fuels compared to diesel allows lower intake of manifold temperature and enhances the volumetric efficiency [58–60]. Figure 8 presents variations in CO emission emitted from the combustion diesel engine using diesel and oxygenated turpentine oil-diesel fuel. In this study, the lowest value of CO emission was found at low engine speeds for both engine loads. Mostly, an increase in engine speed leads to an increase in CO emission. In most operating conditions, CO emission shows a slight increment of 1.2% on average compared to diesel. This is parallel with previous statements. Several studies also reported the same decrements relative to diesel fuel when oxygenated fuel was added into diesel [61–64]. However, at 1600 rpm engine speed, the percentage of CO was increased for both load cases.

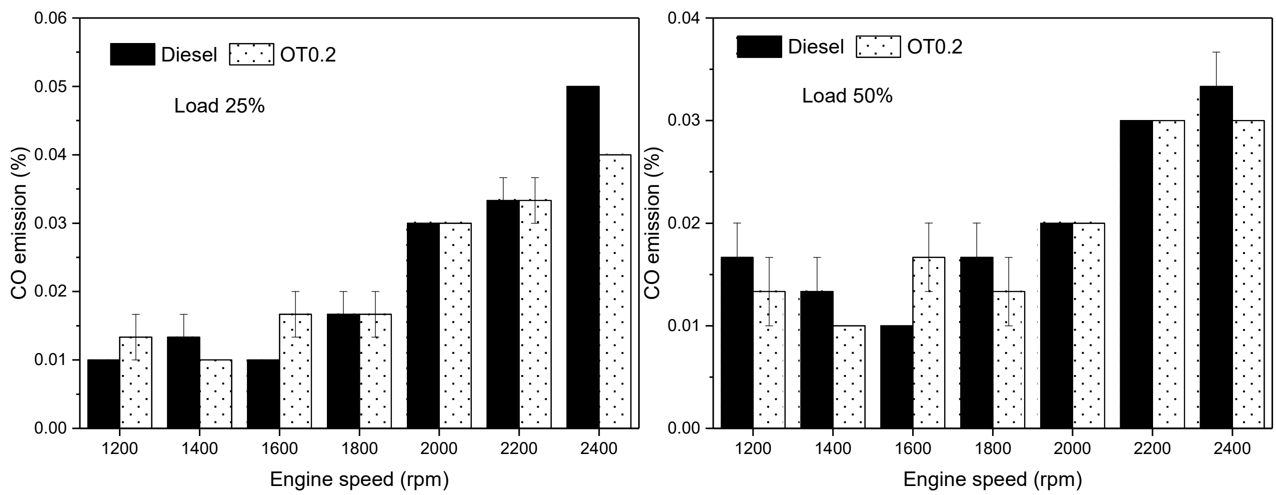


Figure 8. CO emission at various engine speeds.

CO_2 emission is a product of complete combustion. Theoretically, the combustion of hydrocarbon-based fuel should form only two elements, namely CO_2 and H_2O. Figure 9 shows the CO_2 emissions for diesel and oxygenated turpentine oil-diesel fuel at low and medium loads. For both load cases, there are slight increments of CO_2 emissions compared to diesel at most engine speeds. The average increment was 0–37.5% and 0–18% for 25% load and 50% load, respectively. The increase in CO_2 emissions compared to diesel fuel is due to higher average carbon content per energy in oxygenated turpentine. The high oxygen content of additives also leads to an increment of CO_2. The increment aligns with the reported studies [22,56,65].

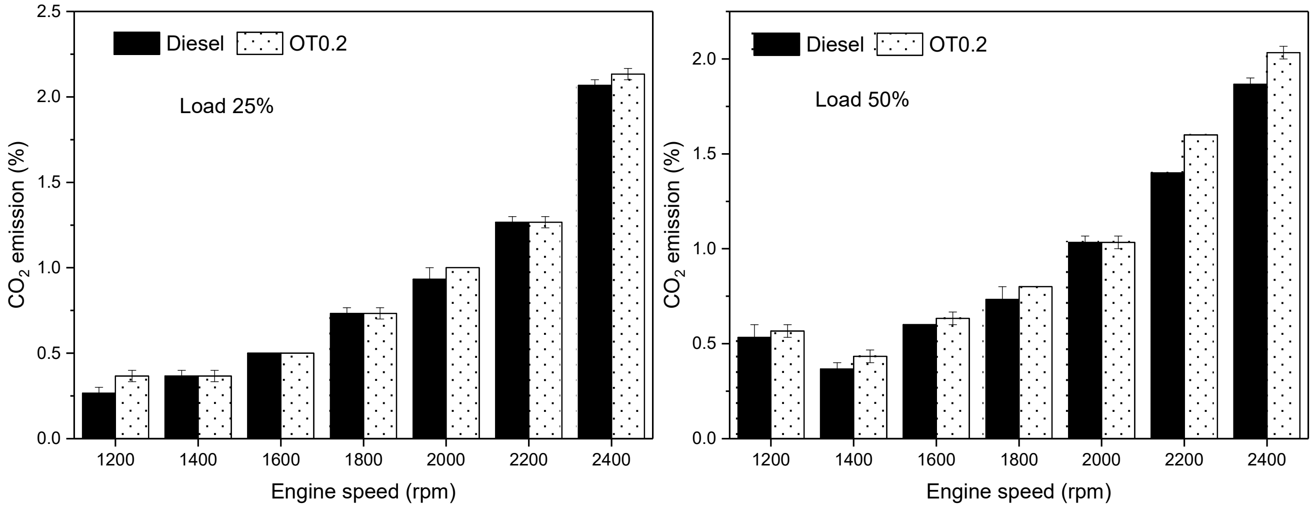


Figure 9. CO_2 emission at various engine speeds.

The major concern of emissions from compression ignition engines is NO_X. Formation of NO_X is strongly related to combustion temperature. It is also connected to engine operation conditions including engine speeds and engine loads, as well as fuel-to-air ratio. Nitrogen reacts with oxygen inside the combustion chamber at high temperatures. At temperatures above 1600 °C, NO_X formation occurs and increases rapidly with increments of temperature [66]. Moreover, NO_X formation happens in the presence of CH radicals at the flame front [67–69]. In this study, generally, there are slight increments of NO_X emission using additives compared to diesel as shown in Figure 10. At 25% load, the range of increment for NO_X emission was 0.5–66% compared to diesel. At 50% load, increments of NO_X emission was 0.3–7.9% relative to diesel. The increment of NO_X formation is due to higher oxygen content in oxygenated turpentine oil-diesel fuel compared to diesel fuel. A similar finding was reported on oxygenated fuel addition in diesel [56,70].

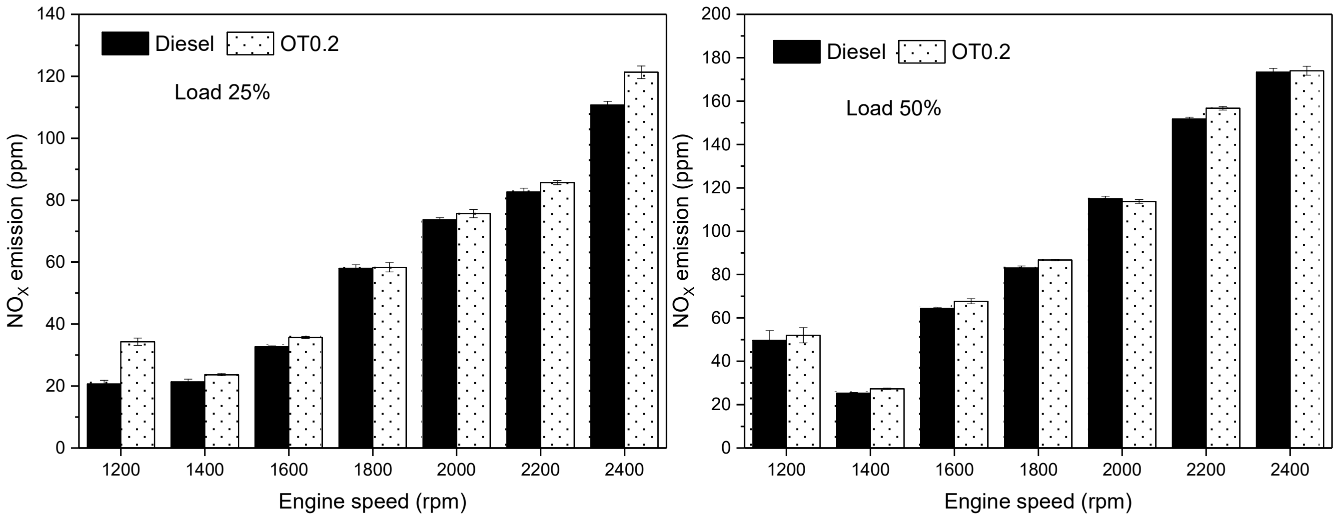


Figure 10. NO_X emission at various engine speeds.

4. Conclusions

The performance and emission of a one-cylinder DI engine using pure diesel and oxygenated turpentine oil-diesel (0.2% vol and 99.8% vol) blend was studied. The addition of oxygenated turpentine into diesel affected the physicochemical properties of the blends including specific gravity, density, aniline point, viscosities, flash point, and stability. The acquired results lead to major conclusions as drawn below.

- The engine power shows slight increments, 0.7–1.1%, whereas the engine torque was slightly decreased using oxygenated turpentine oil-diesel fuel compared to diesel fuel in most conditions.
- The fuel flow rate was lower for OT0.2 compared to diesel in most conditions for low load. The enhancement rate of fuel flow while using an additive is between 5 and 9.09 percent.
- CO emission shows a slight increment when OT0.2 was used, 1.2% on average compared to diesel.
- CO_2 emission increases with OT0.2 usage in diesel fuel up to 37.5%.
- NO_X emission decreased by about 0.3–66% in addition to oxygenated turpentine in diesel compared to diesel fuel.

Therefore, there are a few recommendations for future work and research that could improve and broaden the scope of this experiment. The following suggestions could be used to improve and gain a better understanding of the additive's performance and emission.

- The load applied to the engine could be increased to a high-level load;
- For wider understanding of the effect of oxygenated turpentine to the performance and emission, a larger volume of additive could be tested;
- The application of the additive could be tested in higher power and different types of engines.

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Nomenclature

OT0.2	Diesel fuel + 0.2% of oxygenated turpentine oil
CO	Carbon monoxide
CO_2	Carbon dioxide
NO_X	Nitrogen oxides
HC	Hydro carbons
DI	Direct injection

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