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The Effect of Pistacia Therebinthus L. Oil Biodiesel Blend on Emissions of a CI Engine

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Abstract
In this study, combustion and exhaust emissions of a diesel engine operating with diesel fuel and diesel–biodiesel blends have been investigated. In this study, firstly biodiesel has been obtained from terebinth oil by transesterification method. The viscosity of raw terebinth oil obtained biodiesel was reduced considerably after transesterification. After producing biodiesel from terebinth oil, it was volumetrically mixed with diesel fuel volumetrically 50% and named as B50 fuel. In the secondly, in this study, experiment has been conducted with diesel fuel and B50 fuel in a compression ignition (CI) engine. Compared with conventional diesel fuel, B50 fuel showed lower carbon monoxide (CO), hydrocarbon (HC) and carbon dioxides (CO_2), but higher oxides of nitrogen (NO_x) emissions.

Key words: alternative fuels, terebinth oil, biodiesel, diesel fuel, emission.

1. Introduction

Since the petroleum crises in 1970’s and 1980’s, rapidly increasing of petroleum prices and uncertainties concerning petroleum availability, a growing concern of the environment, and the gases affecting global warming have attracted more interests in the use of vegetable oils as a substitute of diesel fuel. Several studies conducted worldwide have shown that vegetable oil, without any modification on diesel engine, can give performances comparable with those of diesel fuels. The most important advantage of vegetable oils is that they are renewable energy sources compared to the limited resources of petroleum. Many of these studies are on vegetable oils to be used in diesel engines (Labeckas et al. 2005), (Ryu et al. 2004), (Rakopoulos et al 1992), (Lapuerta et al 2005), (Huzayyin et al 2004), (Hebbal et al 2006), (Geyer et al 1984), (Yoshimoto et al 2002). It has been found that the vegetable oils are promising fuels because their properties are similar to diesel and can be produced easily from the crops (Jung et al 2004), (Zou et al 2003), (Nagaraj et al 2002).

Vegetable fuels can be used as an emergency energy source in the event of any petroleum shortage. Extensive studies on alternative fuels for diesel engines have been carried out since the fossil based fuels are limited. Common vegetable oils are sunflower, cottonseed, olive, soybean, corn, nut, linseed, terebinth and sesame oils. The most produced ones in Turkey are sunflower, cottonseed, corn, soybean, olive and nut oils.

Terebinth and other vegetable seeds release oil on compression processes. During the processes of compression of these seeds and final storage, many fatty acids are formed (Gunstone et al 2003), (Bikou et al 2003), (Warner et al 1997), (Yücesu et al 2006). These are palmitic, stearic, oleic, linoleic, arachidic and behenic acids. Terebinth oil also contains some fatty acids like other vegetable oils. The melting point of fatty acids rises with the length of the structural chain of acid. Some vegetable oil contains high concentrations of less common fatty acids. These oils are almost entirely consumed in foods. The excess of these could be used as diesel fuel besides consuming in foods.

Vegetable oil can be used in internal combustion engines, as a fuel. However, ıt has been shown that pure vegetable oils have harmful effects on engine parts and cause a starting up problem (Engler et al 1983), (Schlick et al 1988), (Ramadhas et al 2005), (Muñoz et al 2004), (Bari et al 2002), (Goodrum et al 2005), (Dorado et al 2002), (Krishna et al 2004). The problems due to the viscosity and density of the vegetable oils having different physical and chemical properties from the diesel fuel should be eliminated by making them less viscous. High viscosity of the vegetable oils and its tendency to polymerise within the engine cylinder are major chemical and physical problems encountered. With this aim, it is necessary to obtain either esters or emulsions of vegetable oils (Bhattacharyya et al 1994), (Agarwal et al 2001), (Barnwal et al 2005), (Schwab et al 1987). Vegetable oils can be used as material to produce methyl or ethyl ester. There are several methods for producing of ester; and the best method is known as transesterification (Freedman et al 1986), (Mittelbach et al 1999), (Schuchardt et al 1998), (Ramadhas et al 2005), (İlkılıç et al 2005), (Megahed et al 2004), (Dorado et al 2004), (Encinar et al 2002), (Noureddini et al 1997), (Ma et al 1999), (Harrington et al 1985). Even a blend of 20% biodiesel and 80% diesel fuel will significantly reduce carcinogenic emissions by 27% and gases that may contribute to global warming up (Petrowski, 2002).

In this study, biodiesel was obtained from terebinth oil by transesterification reaction. Then the biodiesel was mixed with diesel fuel by 50% volumetricaly. The blend fuel of B50 was then testified in a diesel fuel in order to find how terebinth oil obtained biodiesel effects on engine combustion and exhaust emission parameters of the engine.

2. Material and method

2.1. Terebinth Plant

Terebinth (Pistacia terebinthus L.), known commonly as terebinth and turpentine tree, is a species of Pistacia, native to the southern and western Turkey. In the eastern shores of the Mediterranean Sea a similar species fills the same ecological niche as this species and is also known as terebinth. It is named as “bıttım” in the area around of Siirt, Turkey.

Pistacia terebinthus is a broad, deciduous bushy tree that grows slowly to the height and breadth of a wide field. It is a small deciduous tree or large shrub growing to 10 m tall. The leaves are compound, the flowers are reddish-purple, appearing with the new leaves in early spring. Its fruit appear like small spherical nutlets and turn brown when mature. The fruit has been eaten as an appetizer in southern Turkey since ancient times. It is used for the treatment of sunstroke, stomachache, gastric ailments, rheumatism, and coughs, and as a stimulant and diuretic in Turkish alternative medicine. It is the source of market products such as dried whole fruit, gummy extract and a special soap, known as “menengic soap” or “bıttım soap”, which contains a different proportion of terebinth oil. All parts of the plant have a strong resinous smell. Physical and chemical properties of terebinth oil used in this study in comparison with other some vegetable oils are given in Table 1.

Table 1. Physical and chemical properties of terebinth oil in comparison with other some vegetable oils

Properties	Terebinth oil	Sunflower oil	Corn oil	Soybean oil
Calorific value (kJ/kg)	39100	39500	37850	39620
Density @ 26°C (Kg/lt)	0.921	0.918	0.919	0.914
Viscosity (mm^2/s) at 26°C	44.85	58	39	65
Flash point (°C)	228	220	277	230
Cetan number	46	37	38	38

2.2. Biodiesel production from terebinth oil

Biodiesel is the monoalkyl ester of long chain fatty acids derived from renewable feedstocks, such as vegetable oil or animal fats, for use in compression ignition engines. Biodiesel is commonly composed of fatty acid methyl esters that can be prepared from triglycerides in vegetable oils by transesterification with methanol. There are no significant differences between the chemical and physical specifications of biodiesel and diesel fuels. Therefore biodiesel can be used in all diesel engines as fuel. The overall transesterification reaction is given in reversible equations as shown in Figure 1.

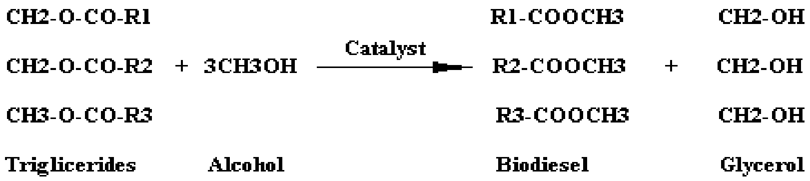

Figure 1. General equation for transesterification.

Methanol containing 1% sulphuric acid (H_2SO_4) can methylise the fatty acids very rapidly. Methanol and oil mixture in a certain proportion can be transformed to biodiesel by holding at 50^{o}C for 12 hours. In particular biodiesel derive by the reaction between triglicerides and methanol. Biodiesel of terebinth oil were prepared with a four molar excess of the alcohol containing 2% H_2SO_4 as catalyst. It had been waited for 12 hours in the bath oil with 50^{o}C. In this study also terebinth biodiesel (TB) was obtained in following way.

The terebinth oil was filled into a flask. An amount of methyl alcohol equal to 50% of prepared oil was mixed with 1% H_2SO_4, volumetrically. Then the mixture of alcohol and H_2SO_4 was added to the flask containing terebinth oil. The mixture was heated and then stired between 50 and 60°C until the oil was completely solved and liquefied in the alcohol. After 12 hours, the reaction products were separated into two layers, the top one was biodiesel and the bottom one was glycerol. The biodiesel layer was separated from glycerol. Then n-hegzan (C_6H_{14}) was added into biodiesel for washing it. The biodiesel was then dried with sodium sulphate (Na_2SO_4). The obtained biodiesel was added to diesel fuel volumetrically by 50%. The fuel mixtures that obtained from the addition of 50% of biodiesel were named here as B50 fuel. The resulting biodiesel is quite similar to conventional diesel fuel in its main characteristics The chemical and physical properties of raw terebinth oil, pure biodiesel (B100), B50 fuel and diesel fuel are presented in the Table 2.

Table 2. Physical and chemical properties of terebinth oil (TO), terebinth biodiesel blend (B50 fuel), terebinth biodiesel (B100 fuel) and diesel fuel (DF).

Parameters	ASTM test no	MO	B50 fuel	B100 fuel	Diesel fuel
Viscosity (mm^2/s)	D445	44,85	3,89	4,12	3,66
Heat value (J/kg)	D2015	39100	41100	40100	43350
Density (15 C) (g/ml)	D1298	0,92	0,86	0,88	0,83
Flash point (°C)	D93	228	69	75	60

3. Experimental Equipments and Test Procedure

Biodiesel was prepared from terebinth oil tested in a following detailed engine in the Table 3.

Table 3. Technical specifications of the test engine

Type and modal	*Rainbow-186 Diesel*
Injection system	Direct injection
Cylinder number	1
Stroke volume	406 cc
Compression ratio	18/1
Maximum power	10 HP (at 3600 rev/m)
Maximum engine speed	3600 rpm ±20
Cooling system	Air cooling
Injection pressure	19.6±0.49 Mpa (200±5 kgf/cm2)
Mean effective pressure	561.6 kpa

Experiments were carried out in Engine Test Laboratory of Automotive Department of Technical Education Faculty at University of Batman, Turkey. The schematic diagram of the experimental setup is shown in Figure 2. Tests were conducted on a single cylinder, four strokes, air cooled diesel engine.

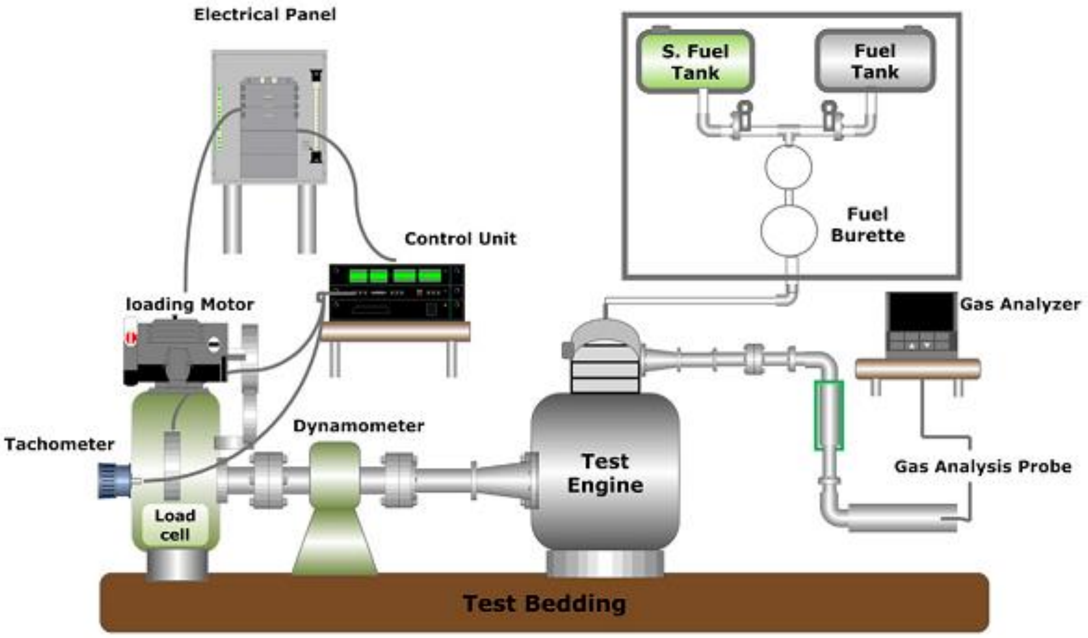

Figure 2. A schematic diagram of the engine setup.

Engine tests were conducted on a BT-140 model hydraulic dynamometer. Technical specifications of the dynamometer control unit and the hydraulic dynamometer are given in Tables 4. The CAPELEC CAP 3200 brand exhaust gas analyzer was used to measure emissions of the test fuels. Percentages of carbon dioxide (CO_2) (%), carbon monoxide (CO) (%), nitrogen oxide (NOx) (ppm), hydrocarbon (HC)(ppm) and oxygen (O_2) (%) were determined by gas analyzer apparatus. The technical specifications of the device have been presented in the Table 5. An infrared temperature measurement device was used to specify exhaust gas temperature.

Table 4. Technical specifications of the dynamometer

Brake motor	*BT-140*
Maximum brake power	50 HP
Maximum speed	7500 rpm
Maximum torque	250 Nm
Capacity of load cell	1000 N
Water consumption for maximum power	V max.. 0.75 m^3/h
Brake water pressure	1–2 kg/cm^2
Brake control type	Slippery propeller
Electricity requirement	220/380 V. 50 Hz

Table 5. Technical properties of the gas analyzing device

Parameter	*Measuring range*	*Precision*
HC	0–20,000 ppm	1 ppm
CO_2	%0–21	%0.1
CO	%0–10.5	%0.001
O_2	%0–21.7	%0.01
NOx	0–10,000 ppm	1 ppm

4. Results and Discussions

4.1. Carbon dioxide (CO_2) emissions

The combustion of fossil fuels produces CO_2, which is getting accumulated in the atmosphere and is leading to many environmental pollution problems. The combustion of biofuels also produces CO_2, but crops are readily absorbing CO_2 and, hence, CO_2 levels are kept in balance. It is very important to observe that, in a global balance, these fuels can limit strongly the rise of CO_2 in the atmosphere because of their vegetable origin.

Carbon dioxide emission is an emission product related to the entire combustion of the fuel. The increase in CO_2 production with diesel fuel must be due to efficient combustion. The high viscosity of B50 fuel must have acted positively to the engine compression and combustion processes. High post-combustion temperature and existence of enough oxygen for an exact burning increase the amount of CO_2. The results of percentage CO_2 emissions of the two fuels are superimposed as shown in Figure 3.

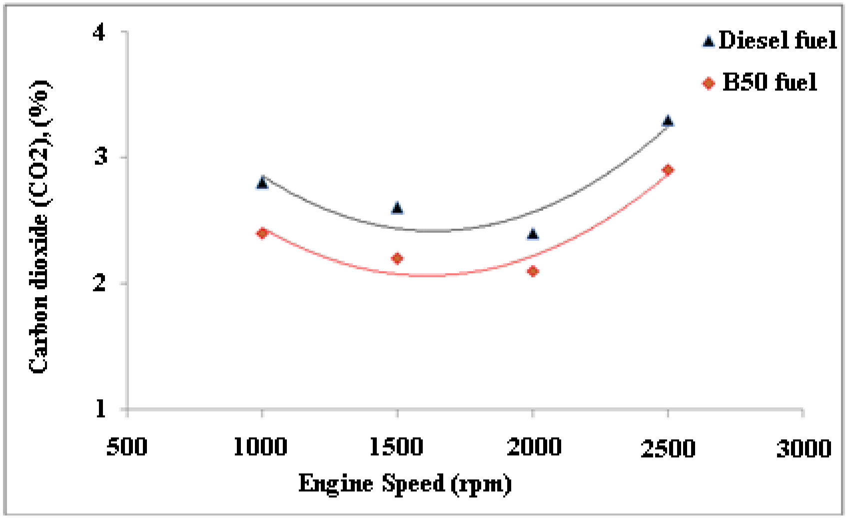

Figure 3. The variation of the carbondioxide (CO_2) at various engine speeds

The CO_2 emission decreased with the increase in engine speed for these two fuels. It is seen from CO_2 amount-engine speed graphics that CO_2 amount is higher around 2500 rpm engine speed for both fuels. It is also understood that the best burning happened near this speed. The CO_2 emission is 3.3% for diesel fuel and 2.9% for B50 fuel at 2000 rpm. One noticeable event is that the emissions of CO_2 appeared to be influenced by fuel viscosity. The emissions of CO_2 were noted to increase as the viscosity increases. It is well known that a decrease in cone angle results in reduction of the amount of air entrainment in the spray. The cone angle in which air entrainment depends, decreases with increased fuel viscosity. This is expected to affect combustion characteristics of the fuel.

4. 2. Carbon monoxide (CO) emissions

HC and CO emissions are main products of incomplete combustion. CO is exerted as a result of inadequate burning and partial oxidation of carbon atoms in fuel. This emission changes depending on the local air/fuel ratio in cylinders. When this ratio is small, the amount of CO increases. As the general trend, the CO emissions fairly reduced when substituting diesel fuel with biodiesel and this can be seen in Fig. 4.

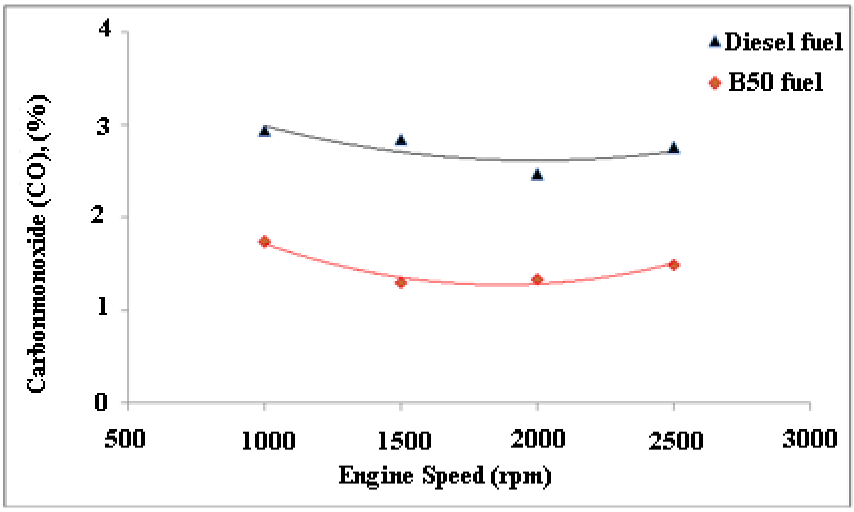

Figure 4. The variation of the carbonmonoxide at various engine speeds

The lowest CO emissions were found for B50 fuel in average. Several reasons can be given for such decrease. Firstly, it may be due to the additional oxygen content in the fuel, which enhances a complete combustion of the fuel, thus reducing CO emissions. When the air is insufficient, CO transforms to CO_2 after a certain amount of air. As can be seen from CO_2-engine speed relationship, CO emission tends to decrease with the increase in engine speed. Secondly, it can be attributed to the higher cetane number of biodiesel fuel that puts the fuel-rich mixture zone away and improves combustion thus reducing CO emissions. Finally, the advanced injection time of biodiesel use due to molecular structure of biodiesel may also explain the reduction in CO emissions. Since turbulence occurs in the combustion chamber at higher speeds, burning improves and due to the increase of the temperature of the mixture, CO emission decreases. When the engine speed decreases and the loading is increased, the quality of burning get worse and CO emission rises. When OH radical which transforms CO to CO_2 decreases below 1500^{o}K, burning deteriorates and consequently, amount of CO increases due to the lower temperature [31].

Figure 4, shows the carbon monoxide emissions for two different fuels under different engine speeds. One can observe from Fig. 5, that the CO emitted by B50 fuel is lower than the ones for the corresponding diesel fuel case. This can be explained by the enrichment of oxygen owing to the biodiesel addition, in which an increase in the proportion of oxygen will promote the further oxidation of CO during the engine exhaust process. As shown in Figure 4, CO emission was lower with B50 fuel compared with diesel fuel for all engine speeds. Similar results were also reported by other researchers (Petrowski, 2002; İlkılıç, 2011; İlkılıç et al., 2010). As can be seen from CO and engine speed relation, CO emission tends to decrease with the increase in engine speed. When the OH radical, which transforms CO to CO_2, decreases below 1500^{o}K, burning deteriorates and, consequently, the amount of CO increases due to the lower temperature as shown in the following equations:

$$CH_3 + O_2 \rightarrow CHO + H_2O \quad (1)$$
$$CH_2 + O_2 \rightarrow CO + H_2O \quad (2)$$
$$CHO + OH \rightarrow CO + H_2O \quad (3)$$

This is typical with all internal combustion engines since the air/fuel ratio decreases with increased load. Since turbulence occurs in the combustion chamber at higher speeds, burning improves and, due to the increase of the temperature of the mixture, CO emission decreases. At the middle speeds of engine test fuels were showed lower CO emissions. It can be attributed to the enriched O_2 in the combustion chamber accompanied by sufficient turbulence created by increased mean piston speed.

When the engine speed decreases and the loading increases the quality of burning gets worse and CO emission rises. It was found that the CO emission decreased with the increase in engine speed. As for higher engine speed there should not be enough time for complete combustion resulted more CO emissions again. One can also observe from this figure that the B50 blend fuel tends to produce lower exhaust CO values than the corresponding ones for the diesel fuel case.

4.3. Hydrocarbon (HC) emissions

The exhaust gasses contain many different HC compounds. The variations of HC emission with engine speed for diesel fuel and B50 fuel is presented in the Fig. 5.

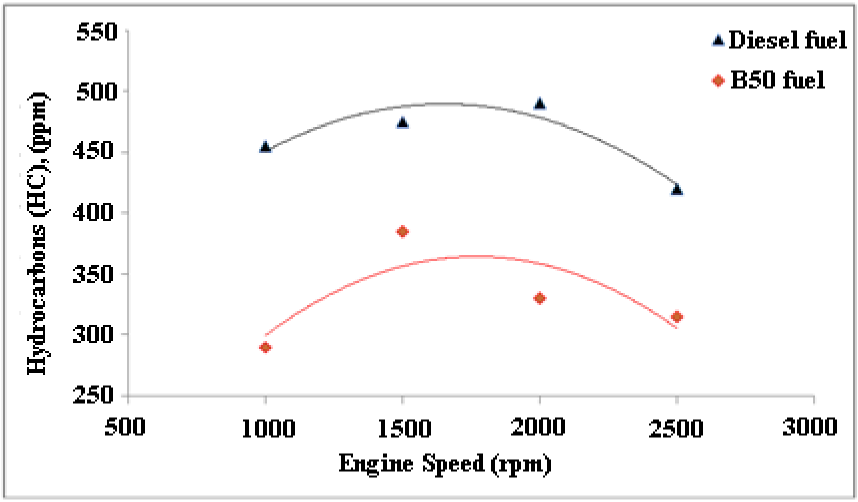

Figure 5. The variation of the hydrocarbon emissions at various engine speeds

The figure shows the comparison of the results of B50 fuel with the baseline diesel fuel. B50 fuel operation produced the considerably lower HC emissions compared to the results of diesel fuel. The HC emission which is one of the organic compounds is formed in the result of incomplete combustion. HC emissions fairly increase in the case of richer fuel–air ratios above the stoichiometric ratio. Besides, in the excessively leaned fuel–air ratio conditions, due to incomplete combustion that resulted from the lack of oxygen, HC emissions rapidly increase again. Normally, as the fuel viscosity is decreased, the penetration rate decreases and the spray cone angle increases. With B50 fuel, the penetration rates increased as the viscosity was reduced by increasing the temperature of the biodiesel. The HC emissions were noted to increase with decreased fuel viscosity. In many cases, the HC emissions for B50 fuel have been reported lower than that of diesel fuel. It can be attributed to the oxygen content in the biodiesel molecule, which leads to a more complete and cleaner combustion. Also, the higher cetane number of diesel fuel shortens the combustion delay and thus reduces HC emissions.

4.4. Nitrogen oxides (NOx) emissions

Nitrogen oxide is the generalized term for NO and NO_2 given with the formulae of NOx. NOx is formed as a result of the oxidation of nitrogen in the air during burning of the air-fuel mixture in the combustion chamber. Its formation is dependent on the duration of the flame temperature in the combustion chamber above 1800°K [32]. The test results showed an increase in NOx emission when using B50 fuel. The obtained increase in NOx emissions was in proportion to the biodiesel concentration in the blend as can be seen in Fig. 6.

When the burning temperature is above 1800°K, NOx formation considerably accelerates. The lowest NOx emissions were obtained with using diesel fuel and the highest NOx emissions were obtained with B50 fuel. The main reason for NOx increase is the oxygen content of biodiesel which improves combustion thus increases the temperature and resulting NOx production reaction which occurs after 1800°K. In the formation of nitrogen oxides, the prodominant factors are the air/fuel ratio and the environment temperature. In case of adequate burning the temperature rises and consequently more free oxygen atoms combine with nitrogen thus increasing the formation rate of nitrogen oxide. In poor mixtures, first O_2 is decomposed to 2O. Then it is accepted that NO forms with free radicals. Another argument is the increased cetane numbers of biodiesel which leads to advanced combustion by shortening ignition delay which promotes NOx formation reactions. Since the activation energies of these reactions are high, both reactions in lower temperatures are very slow. Since cetane number of biodiesel increases in proportion to the concentration of biodiesel in the blend, B50 blend resulted in the highest NOx emission. As can be seen from Figure 5, at first the increase in NOx emission for both fuels with the increase in engine speed and then decrease after a certain speed support this. From both graphics of emissions, it is seen that the best burning is in the maximum torque range. This also means that the maximum temperature is reached in this range and NOx emissions are higher.

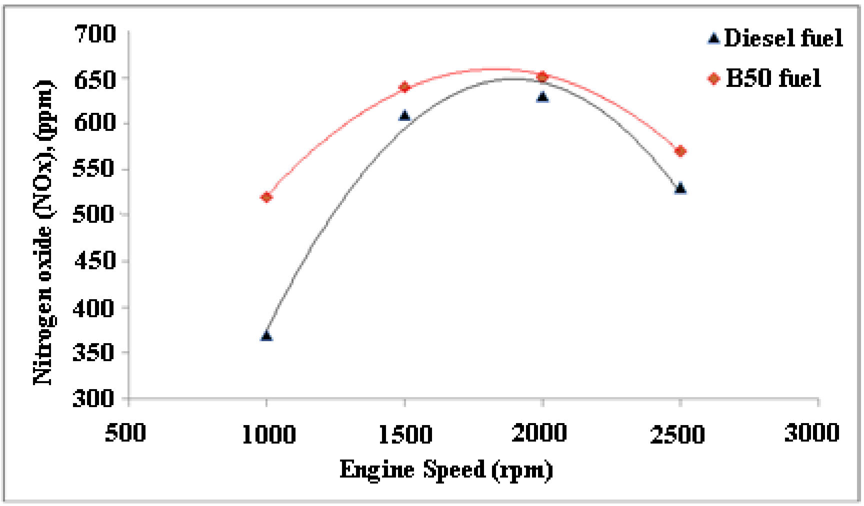

Figure 6. The variation of the nitrogen oxide at various engine speeds

4.5. Oxygen (O_2) emissions

The amount of power an engine can produce is limited by how much fuel it can burn, and the amount of fuel it can burn is limited by the amount of air in the engine cylinder. The air is composed of oxygen and nytrogen. The amount of oxygen in the engine cylinder is limited by the amount of air in the cylinder. Increasing the oxygen flow to the diesel engines reduces particulate emissions and increases engine power output. The oxygen (O_2) emission for B50 fuel and diesel fuel as the engine test fuels under varied engine speeds are shown in Figure 7.

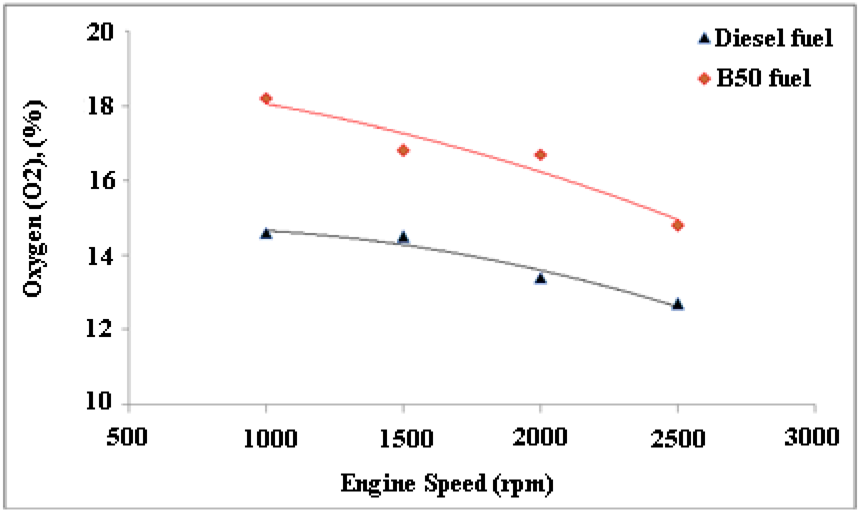

Figure 7. The variation of the oxygen emissions at various engine speeds

The variations of oxygen (O_2) for running the diesel engine by B50 fuel was compared with that by diesel fuel in this figure. The amount of oxygen decreases from 14.6% to about 12.7% when the engine speed is increased from 1000 rpm to 2500 rpm for diesel fuel. In the case of B50 fuel, it is seen that O_2 emission is higher in all engine speeds. This means that the B50 fuel contains more oxygen than diesel fuel.

4.6. Exhaust gas temperature

The variation of the exhaust gas temperatures of the test fuels were evaluated on a graph. The exhaust temperatures of the engine when using diesel fuel and B50 fuel were presented in the Fig. 8.

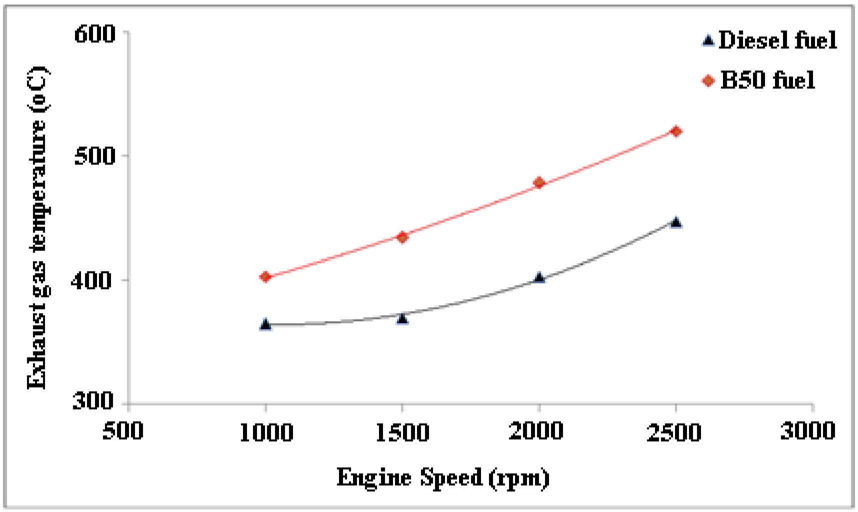

Figure 8. The variation of the exhaust gas temperature at various engine speeds

Exhaust gas temperatures of the fuels changes change with the factors such as viscosity, heat capacity and flame velocity during burning. Low viscosity causes poor atomization which leads to the longer ignition times and continuation of burning in the expansion stroke. Consequently, post burning pressure and temperature become lower. The exhaust temperature increased almost linearly with the increase in engine speed for both test fuels. It can be seen clearly in the Fig. 6 that the higher temperature values were obtained for biodiesel blend and the increase was observed the highest for B50 fuel. At higher engine speeds, spreading of the burning in the exhaust system causes the temperature of the exhaust gases to rise. If the heat capacity of the fuel is high, the energy exerted during combustion gets higher and subsequently the energy of the exhaust gas is higher. It can be attributed to the more complete combustion for biodiesel use thanks to the oxygen that was inherently contained in the biodiesel.

5. Conclusions

In this study, an alternative biodiesel fuel was obtained from terebinth seed oil by the transesterification method. Some of important physical and chemical fuel properties of the oil, pure biodiesel and biodiesel blend (B50) fuel as well as diesel fuel were found. By the production process, the viscosity and density of the oil decreased while the calorific value slightly increased. While the density and viscosity of biodiesel fuel decreased from 0.92 kg/l to 0.86 kg/l and from 44.85 mm^2/s to 3.89 mm^2/s respectively at 26°C, the heat capacity increased from 39100 kJ/kg up to 41100 kJ/kg. B50 fuel produced has more similar properties to diesel fuel compared with terebinth oil.

Carbon dioxide emissions measured in the experiments with diesel fuel are higher than that of B50 fuel for all the engine speeds. CO_2 decreased by 31% when B50 fuel was compared to diesel fuel. Maximum CO_2 emission was measured at the engine speed of 2500 rpm for the maximum engine power for both fuels. CO was reduced by 47% when B50 fuel was compared to diesel fuel. The same results are not valid for NOx emission. Nitrogen oxide emission for B50 fuel was increased when it was compared with diesel fuel. NOx and CO_2 emissions are maximum in the range of maximum burning efficiency. Considered exhaust emissions it can be concluded that B50 fuel is superior to diesel fuel. All these arguments showed that due to the improved combustion with the use of biodiesel, it made the performance of the engine remain higher than expected. The positive effects of B50 fuel were found in the reducing of CO, HC and CO_2 emissions. As a result, B50 fuel is less toxic, more biodegradable, has no harmful effects on bio life, and it is environmentally friendly. It is one of the most important fuels for reducing greenhouse gases and, thus, it is suited to global warming to maintain and follow the Kyoto Protocol.

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