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The Effect of Terebinth oil Methyl Ester on Engine Performance and Exhaust Emissions in a Diesel Engine

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ABSTRACT: In this study, exhaust emissions and performans of biodiesel from terebinth oil in a compression ignition engine was experimentally investigated. In the investigation, firstly biodiesel from menengic oil has been obtained by transesterification method. The viscosity of raw menengic oil biodiesel, obtained after transesterification, was reduced considerably and heating value was improved. After producing biodiesel from menengic oil, it volumetrically mixed with diesel fuel as a named B10 fuel. In the second phase of this investigation, experiment has been conducted with neat diesel fuel and biodiesel blend (B10 fuel) in a four stroke compression injection (CI) diesel engine. Compared with conventional diesel fuel, diesel–biodiesel blends showed lower engine power,engine moment,carbon monoxide (CO), hydrocarbon (HC) and carbon dioxides (CO2) but higher oxides of nitrogen (NOx) emissions. Keywords: Alternative fuels; Menengic oil; Biodiesel; Diesel fuel; Emissionn CI engines.

Keywords: Alternative fuels, diesel fuel, emission, terebinth oil biodiesel

Menengiç yağı Metil Esterinin Bir Dizel Motorunda, Motor Performansı ve Egzoz Emisyonlarına Etkisinin Araştırılması

ÖZET: Bu çalışmada menengiç yağı biyodizeli egzoz emisyonu ve motor peformansı sıkıştırma ateşlemeli bir motorda deneysel olarak incelenmiştir. Araştırmada, ilk olarak menengic yağından transesterifikasyon yöntemi ile biyodizel elde edilmiştir. Transesterifikasyon işleminden sonra ham menengic yağı biyodizeli viskozitesi önemli ölçüde azaltılmış ve Isıldeğerinin yükseldiği görülmüştür.Elde edilen biyodizel hacimsel olarak olarak %10 olarak saf dizel yakıtı ile karıştırıldı. (B10).Araştırmanın ikinci aşamasında Dizel yakıtı ve Dizel Biyodizel karışımı (B10) dört zamanlı sıkıştırmalı enjeksiyon motorunda denendi. Geleneksel dizel yakıt ile karşılaştırıldığında, diesel–biodiesel karışımlar yüksek Azot oksit (NOx) emisyonları daha düşük motor gücü,motor torku karbon monoksit (CO), hidrokarbonlar (HC) ve karbon dioksit (CO2) değerleri verdiği görülmüştür.

Anahtar kelimeler: Alternatif yakıtlar, biyodizel, dizel yakıt, emisyon, menengic yağı

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INTRODUCTION

The high cost of petroleum and petroleum crises have brought much pressure on many countries to re-evaluate their national energy strategies. Ever since the petroleum crises of the 1970s, 1980s and 1992s, there has been an incentive to increase energy security by seeking substitutes for petroleum. There are several possible alternative sources of fuels namely vegetable oils, alcohols such as methanol and ethanol, gases such as CNG, liquefied petroleum gas LPG for substitute's engine fuels. In the past, many investigations have been carried out on the use of vegetable oils as diesel fuel. Vegetable oils are alternative fuels and many researches are carried out on development of these fuels. The acceptability of vegetable oils as diesel fuel has been evaluated for the first time in the 70th years because of the well known energy crises. Several studies conduced world-wide have shown that vegetable oil, without any modification on diesel engines, can give engine performances comparable with those of diesel fuels. In general, it has been reported by most researchers that if crude vegetable oils are used as diesel engine fuel (Huzayyin and He, 2005). The most important advantage of vegetable oils is that they are renewable energy sources compared to the limited resources of petroleum.

Extensive studies on alternative fuels have been carried out since the fossil based fuels are limited. One of these studies has ever been on vegetable oils to be used in diesel engines. However, using raw vegetable oils for diesel engines can cause numerous engine related problems. To solve these problems caused by the very high viscosity of neat vegetable oils, the following usual methods are used. These methods are pre-heating, micro emulsification with methanol or ethanol, blending in small blend ratios with normal diesel fuel, and converting them into biodiesel fuels. The increased viscosity and low volatility of vegetable oils lead to severe engine deposits, injector chocking and piston ring sticking. In the researches done so far, some negative sides of using vegetable oils in engines such as carbon deposits in combustion chamber, harmful effects on engine parts, clogged injectors, needle adhesion and the cause a first starting problem have been observed (Dorado **and** Pestes ,2005). In addition, decrease in combustion efficiency due to poor atomization, thickening of lubricant and piston and ring adhesion has also been reported by some researchers (Barnwal and Bhattacharyya 1994). The problems due to the viscosity and density of the vegetable oils having different physical and chemical properties from of the diesel fuel should be eliminated to make them less viscous. However, these effects can be reduced or eliminated through transesterification of vegetable oil to form methyl ester. Although vegetable oils are all virtually sulphur-free, they create other problem in that they are generally too viscous, often acidic, they choke injector nozzles with carbon and leave high carbon residue on burning (Agarwal and Dorado, 2004). In studied works was noted some problems as a result of using plants oil and as a fuel blends. One of these problems, a thickening of crankcase oil, has occurred which is attributed to the contamination of petroleum – based crankcase oil with unburned raw plant oil. Second problem, a build up of carbon on and in fuel injector nozzles and piston rings was observed. However, a great deal of research has been done into blends with petroleum-derived fuel and into the use of vegetable oil esters. There is always an immixing gap when vegetable oils are mixed with diesel fuel due to the difference in densities. With this aim, it is necessary to obtain esters or emulsions of vegetable oils (Gunstone and Mittelbach. 2003). It had been made short and long term engine performance and emission tests using vegetable oil methyl or ethyl ester (biodiesel) fuel for high speed diesel engines. The use of biodiesel is rapidly expanding around the world, making it imperative to fully understand the impacts of biodiesel on the diesel engine combustion process and pollutant formation.

Biyodiesel have been prepared from terebinth oil and compared their fuel properties to Turkish standards. Terebinth oil was transesterified using alkaline catalyst and it has been noted that all specification values could be met by the use of vegetable oil esters. Terebinth oil is attracting considerable attention as diesel fuel extenders of substitutes either in the form of the transesterified-chemically modified terebinth oil-with various monohydric alcohols. Some vegetable oil contains high concentrations of less common fatty acids (Klopfenstein, 1983). These are palmitic, stearic, oleic, lynoleic, arachidic, and behenic acids. Like the others, terebinth oil includes acids in its content as well. The chemical formulations and the percentage of these fatty acids are available in the literature. Chemical compositions of terebinth oil indicate that this is a suitable alternative diesel fuel. Physical properties of terebinth oil and some other vegetable oils are shown in following Table 1. As can be seen in the Table 1, Physical and chemical properties of terebinth oil has compared to some other vegetable oils have.

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^{o}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	36	38

Vegetable oil or animal fats can be converted to ester by removing the last carbon in chain and replacing methyl in the place or in another word the methyl ester (biodiesel) of that oil is obtained (İlkılıç,2011).

Terebinth oil was converted to biodiesel through transesterification. The transesterification procedure was conducted by heating the oil to 50^{o}C. For one litre of Terebinth oil, an amount of 9 g of NaOH was added to 220 mL of methanol and mixed. The mixture was added to the oil and mixed for 50 minutes. After 12 hours, the oil phase was separated to another flask and centrifuged to remove the glycerin produced. The biodiesel was then washed with 500 mL of water. After one hour, another washing with 500 mL of water was conducted. The mixture of biodiesel and water was centrifuged to remove all the remaining water from the biodiesel The overall transesterification reaction is given in reversible equations as shown in Figure 1.

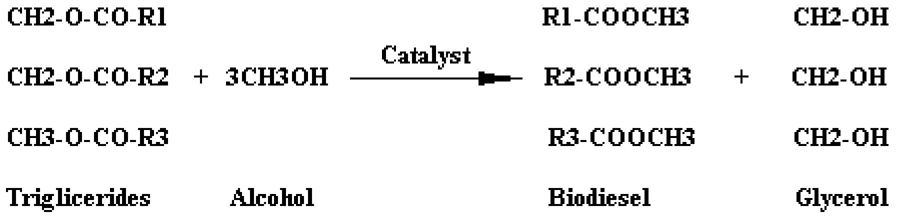

Figure 1. General equation for transesterification

There are some differences between the properties of the oil and its own ester. The essential difference is in viscosity and density. After transesterification the viscosity and density become closer to of the diesel fuel. Due to the high viscosity, large drops are formed and consequently combustion becomes difficult as a result the amount of HC and soot increase (Christie, 1989). Different properties of crude terebinth oil (TO), Biodiesel blend (B10 fuel), pure diesel fuel (B100 fuel) and diesel fuel (DF) are shown in Table 2.

Table 2. Physical and chemical properties of terebinth oil (TO), terebinth biodiesel blend (B10 fuel), terebinth biodiesel (B100 fuel) and diesel fuel (DF)

Parameters	**ASTM test no**	**TO**	**B10 fuel**	**B100 fuel**	**Diesel fuel**
Viscosity (mm^2/s)	D445	44,85	3,70	4,12	3,66
Heat value (J/kg)	D2015	39100	432514	40100	43350
Density (15 C) (g/ml)	D1298	0,92	0,83	0,88	0,83
Flash point (°C)	D93	228	62	75	60
Cetane index	D613	46	56	55	57

Experimental setup and procedure of experimentation

A mixture was prepared in laboratory conditions, 10% biodiesel with 90% diesel fuel volumetrically (B10 fuel), and tested in a one cylinder, four-stroke, direct injection, air cooled Rainbow-186 Diesel engine with a compression ratio of 18:1.

The engine was a commercial diesel engine and it was coupled with a dynamometer. Technical specifications of the test engine are shown in Table 3. All experiments were conducting at standard temperature and pressure.

The engine speed was measured directly from the tachometer attached with the dynamometer. The engine out NOx, HC, CO_2, O_2 and CO was measured with a digital gas analyzer device.

The CAPELEC CAP 3200 brand exhaust gas analyzer was used to measure emissions of the test fuels. The technical specifications of the device have been presented in the Table 4.

The tests were performed with maximum gas and at different engine speeds and engine powers. The aim of this study was to investigate the effect of terebinth based oil biodiesel blend with diesel fuel on the exhaust gas emissions of compression engine (CI).

The engine was operated on diesel fuel first and then on B10 fuel. Tests were held on a laboratory test bed which consisted of an electrical dynometer, an exhaust gas analyzer, a data acquisition system and engine mounting elements, as shown in Fig. 1. Prepared biodiesel from terebinth oil in laboratory conditions was mixed volumetrically 10% with diesel fuel (B90 fuel) and tested in a following detailed engine.

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.

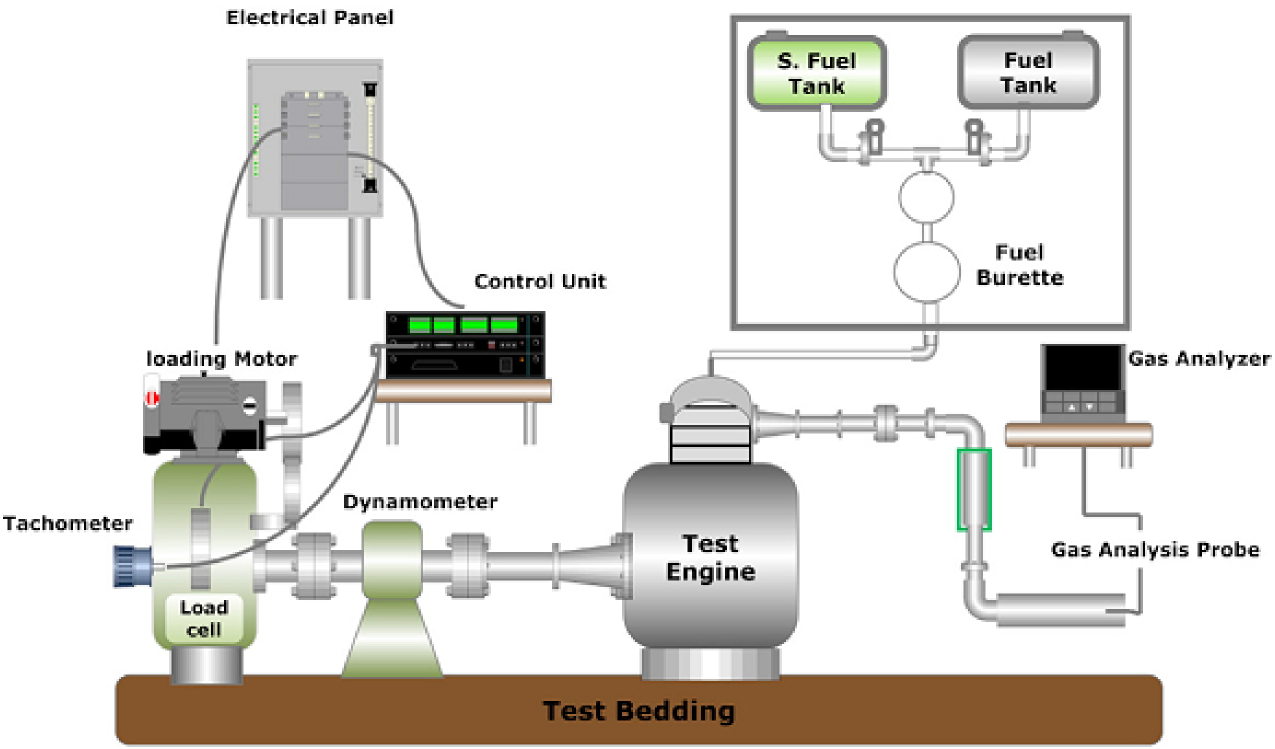

Figure 2. A schematic diagram of the engine setup

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
Medium piston speed	7.0 m/s (at 3000 rpm)

Table 4. 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

RESULTS AND DISCUSSION

Engine Torque

The level of torque observed with the Diesel fuel and B10 mixtures at full engine speed and different rpm levels are shown in Figure 8. At lower rpm values, the engine torque for both the Diesel fuel and B10 fuels were relatively lower, while increasing the rpm to values above 1500 lead to the maximum torque values for both fuels. Both types of fuel reached their minimum torque values at 2500 rpm, with a value of 23,56 Nm being measured for Diesel fuel, and a value of 22,55 Nm being measured for B10. The diesel fuel had higher engine torque values than the B10 fuel at 1500, 2000 and 2500 rpm levels.

This was possibly associated with the better combustion performance of the diesel fuel than the B10 fuel.

Effective Engine Power

The effective engine power levels observed with the Diesel fuel and the B10 mixture at full engine speed and different rpm levels are shown in Figure 9. Figure 9 indicates that the B10 fuel produced less effective engine power than the Diesel fuel. The effective power output of the engine increased parallel with the increase in rpm. This parallel increase in effective engine power and rpm was due to the increase in number of revolutions/cycles per time unit. Both types of fuel reached their maximum effective engine power value at 2500 rpm, with a value of 6.2 kW being measured for DF, and a value of 6.1 kW being measured for B10.

Carbon monoxide (CO) emissions

Carbon monoxide (CO) is an intermediate combustion product and is formed mainly due to incomplete combustion of fuel in the combustion chamber or CO emission is exerted as a result of inadequate burning and partial oxidation of carbon atoms in fuel. If combustion is complete, CO is converted to CO_2. If the combustion is incomplete due to shortage of air or due to low gas temperature, CO will be formed.

This emission changes depending on the air/fuel ratio in cylinder. When this ratio is small, the amount of CO increases. Figure 3 shows the CO emissions of the diesel fuel and the B10 fuel.

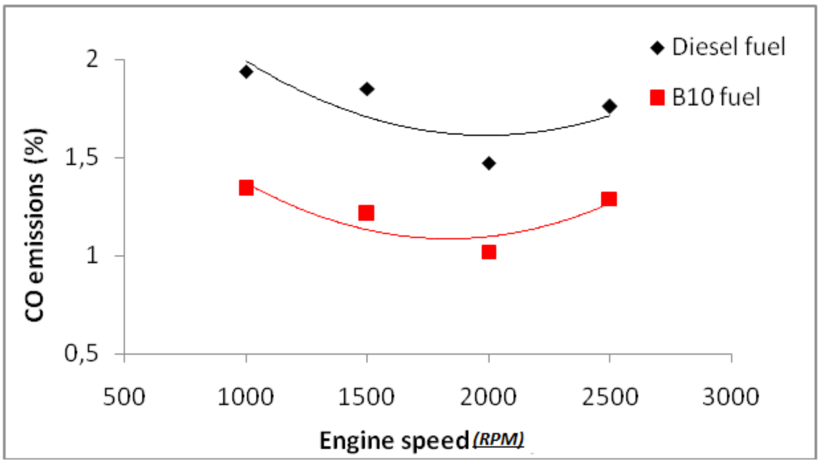

Figure 3. The variation of the carbonmonoxide (CO) emissions at the various engine speed.

When the air is insufficient, CO transforms to CO_2 after a certain amount of air. Usually high diesel CO emissions formed with fuel-rich mixtures, but as diesel combustion is occurred with lean mixture and has an abundant amount of air, CO from diesel combustion is low. When OH radicals which transform CO to CO_2 decreases below 1500°K, burning deteriorates and consequently, amount of CO increases due to the lower temperature. The comparative analysis of CO is shown in Figure 3. Comparing diesel fuel and B10 fuel, relatively lower CO emissions were obtained with B10 fuel. Since turbulence occurs in the combustion chamber at higher speeds high power, burning improves, and due to the increase of the temperature of the mixture, CO emission decreases. When the engine speed decreases and the loading increases the quality of burning gets worse and CO emission rises.

The partial oxidation of B10 fuel causes CO emission to be relatively lower than of the diesel fuel. In the experiments performed with B10 fuel, CO emissions were determined to have decreased by 26-47%. For B10 fuel CO emission was lower than that of diesel fuel, because B10 fuel contains some extra oxygen in their molecule that resulted in complete combustion of the fuel and supplied the necessary oxygen to convert CO to CO_2. Compared to diesel fuel, B10 fuel reduced CO emissions about by 20%.

Carbon dioxide (CO_2) emissions

The variations of CO_2 emissions related to both two fuels are shown in Figure 4. Carbon dioxide (CO_2) emission is an emission product related to the entire combustion of the fuel in the engine combustion chamber. In case of diesel fuel it can be seen in Figure 4 that CO_2 emission is higher at all engine speeds.

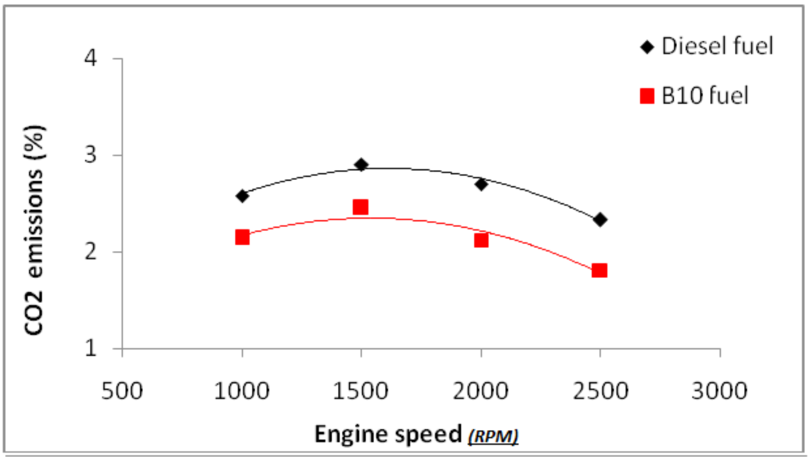

Figure 4. The variation of the carbon dioxide (CO_2) emissions at the various engine speed.

This means that the quality of combustion for diesel fuel is higher than B10 fuel.

This is an expected result of relatively better spraying qualities and more uniform mixture preparation of air and diesel fuel.

High post-combustion temperature and existence of enough oxygen for an exact burning increase the amount of CO_2. However, at all of the engine speeds, the diesel fuel showed a marginal increase in CO_2 emissions over B10 fuel.

It is seen from CO_2 amount–engine speed graphics that CO_2 amount is higher around 1500 m/s speed for both fuels.

It is also understood that the best burning occurred around this speed. The CO_2 emission is 3.2% for diesel fuel and 2.6% for B10 fuel at 1500 m/s.

The CO_2 emission is 2.78% for diesel fuel and 2.30% for B10 fuel at 2000 m/s engine speed. CO_2 emission is seen to be 2.63% for diesel fuel and 1.74 for B10 fuel at 2500 m/s engine speed.

Hydrocarbon emissions

The exhaust gasses contain many different hydrocarbons (HC) compounds. Hydrocarbons are organic compounds that consist of only C and H atoms. The HC emission which is one of the organic compounds is formed in the result of incomplete combustion. When hydrocarbons burn in sufficient oxygen, carbon dioxide and water are the sole products. The total unburned hydrocarbons were measured as "ppm" with the gas analyzer. Hydrocarbons are molecules that contain hydrogen and carbon and come in various lengths and structures, from straight chains to branching chains to rings. The main structural difference among hydrocarbon families is the presence of double or triple bonds between carbon atoms. The alkanes are saturated organic compounds, or those with only single bonds. Unsaturated organic compounds are those which have double or triple bonds.

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.

The variations of HC emission with engine speed for diesel fuel and B10 fuel is presented in the Figure 5, and the figure shows the comparison of the results of B10 fuel with the baseline diesel fuel.

B10 fuel operation produced the highest HC emissions compared to the results of diesel fuel. Normally, as the fuel viscosity is decreased, the penetration rate decreases and the spray cone angle increases. With B10 fuel, the penetration rates increased as the viscosity was reduced by increasing the temperature of the biodiesel. HC emissions were noted to increase with decreased fuel viscosity. In many cases, the HC emissions for B10 fuel have been reported higher 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. The higher cetane number of diesel fuel shortens the combustion delay and thus reduces HC emissions. However, at high and low engine speed, and combustion temperature, B10 fuel showed an increase HC emission over the diesel fuel.

Nitrogen oxide emissions

Nitrogen oxide (NOx) is the generalized term for NO and NO_2 given with the formula of NOx. The composition of NO_x emitted from a combustion system consists of nitrogen monoxide (NO) and nitrogen dioxide (NO_2), particularly the former. Naturally NOx emission increases with the increase in engine torque. It is well known that nitrogen is an inert gas, but it remains inert up to a certain temperature (1100^oC) and above this level it does not remain inert and participate in chemical reaction. NOx emissions are usually resulting in higher combustion temperatures. Its formation is dependent on the duration of the flame temperature in the combustion chamber above 1800^oK. At this temperature oxidation of nitrogen takes places in presence of oxygen inside the combustion chamber. In the formation of nitrogen oxides, the prodominant factors are the air/fuel ratio and the environment temperature. An increase in the engine speed reduced the NO*x* concentration considerably. In the case of adequate burning the temperature rises and consequently more free oxygen atoms combine nitrogen and this, in turn, increases the formation rate of nitrogen oxide. On the other hand, since the formation of nitrogen oxides do not attain chemical equilibrium reaction; then after the end of expansion stroke when the burned gases cool and the formation of NOx freeze, the concentration of the formed NOx in the exhaust gas remain unchanged. When the burning temperature

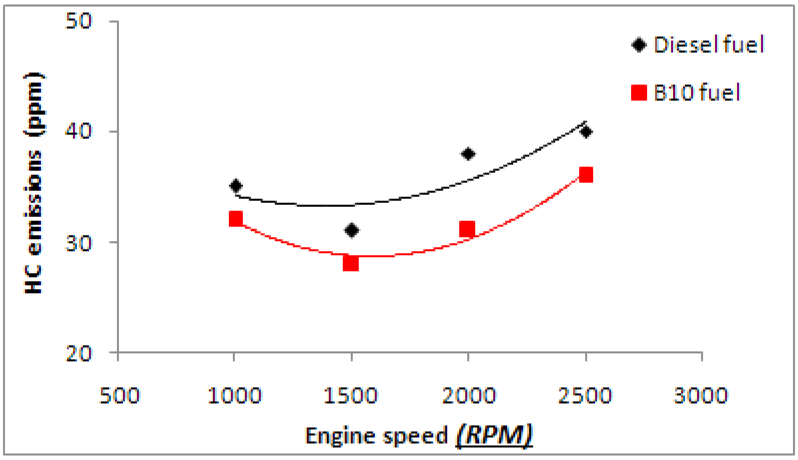

Figure 5. The variation of the hydrocarbon (HC) emissions at the various engine speed.

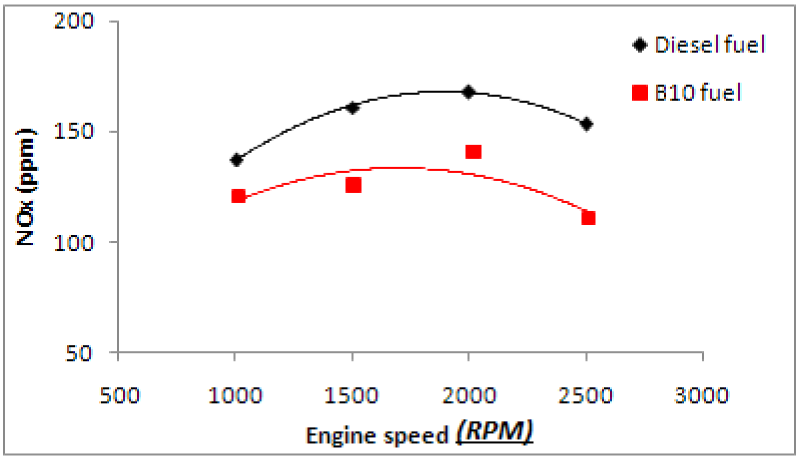

Figure 6. The variation of the nitrogen oxide (NOx) at the various engine speed.

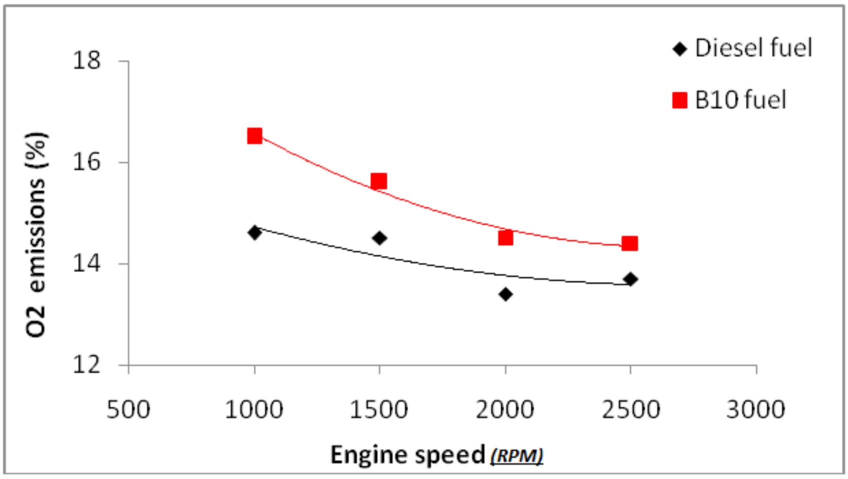

Figure 7. The variation of the oxygen (O_2)emissions at the various engine speed.

is above 1800°K, NOx formation considerably accelerates. NOx formation changes as dependent upon the air surplus coefficient.

When air surplus coefficient is higher, the cooling rate of engine decreases and the exhaust system remains hot. In poor mixtures, first O_2 is decomposed to 2O. It is then accepted that NO forms with free radicals. The effect of the gas temperature on NO*x* production becomes more dominant, based on the extended Zeldovich thermal NO mechanism, for larger engine speeds. Since the activation energies of these reactions are high, both reactions in lower temperatures are very slow. As can be seen from Figure 6, initially the increase in NOx emission was, for both fuels, with the increased in engine power and then decreased. Fig. 6 also shows that NOx level was higher for biodiesel mixtures than conventional diesel fuel at the same engine speed.

This can be explained due to the presence of extra oxygen in the molecules of biodiesel mixtures. This additional oxygen was responsible for extra NOx emission.

From both graphics of emissions, it is seen that the best burning was at the 2000 m/s engine speed. This also means that the maximum temperature is reached in this range and NOx emissions are higher.

As seen in Figure 6, NOx emissions are lower for all engine speeds in case of B10 fuel. It was 168 ppm with diesel fuel, whereas 120 ppm for B10 fuel at 2000 m/s engine speed.

Reduction of NOx with biodiesel may be possible with the proper adjustment of injection timing and introducing to exhaust gas recirculation (EGR).

Oxygen Emissions

The amount of power that 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 oxygen in the engine cylinder. 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. Figure 7 shows the oxygen emission concentrations for varying engine speeds. The variations of oxygen (O_2) for running the diesel engine by B10 fuel was compared with that by diesel fuel in that figure. The O_2 emissions were reduced nearly linearly with increasing engine speeds. A greater fuel consumption rate was required for greater engine speeds. This leads to a larger fuel to-air ratio under a constant inlet-air consumption rate. Hence, lower excess oxygen was produced under a higher engine speeds.

The amount of oxygen decreased from 16.6% to about 15.2% when the engine speed was increased from 1000 m/s to 2000 m/s for diesel fuel. From engine speed was increased 1000 m/s to 2000 m/s, O_2 decreased from 14.2% to about 13.4% for B10 fuel. In the case of B10 fuel, it is seen that O_2 emission was higher at all engine powers. This means that the B10 fuel contains more oxygen than diesel fuel.

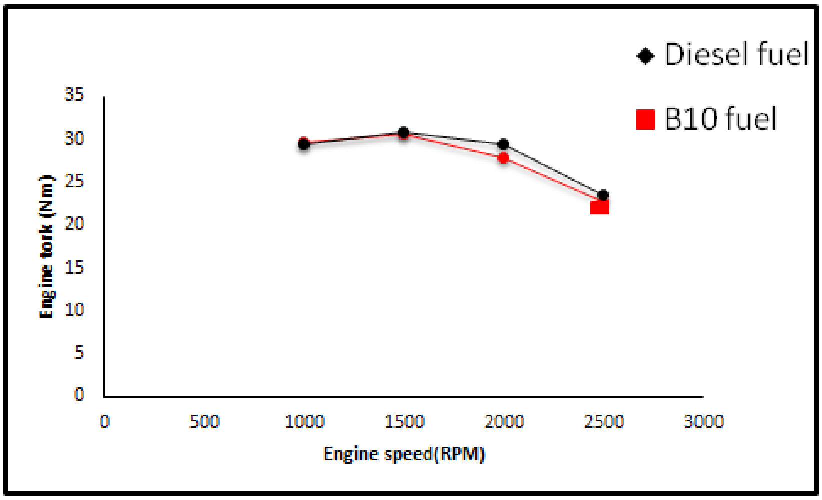

Figure 8. The variation of the torque (Nm) at the various engine speed.

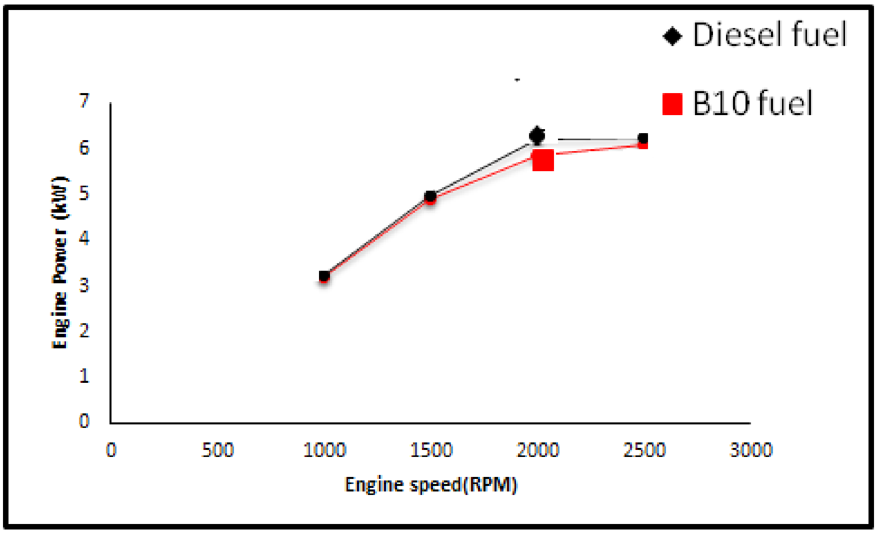

Figure 9. The variation of the torque (Nm) at the various engine speed.

CONCLUSIONS

In this study, an alternative biodiesel fuel was produced from terebinth seed oil by the transesterification method. By the production process, the viscosity and density of the oil decreased while the calorific value slightly increased. The production of B10 fuel from terebinth oil may simultaneously reduce dependence on imported fossil fuels. Some of important physical and chemical fuel properties of the oil, pure biodiesel and biodiesel blend fuel as well as diesel fuel were found. It was found that the fuel properties of the biodiesel and biodiesel blends were fairly similar to that of diesel fuel. For the study, the effect of terebinth oil biodiesel-diesel fuel blends (B10 fuel) and diesel fuel on engine exhaust emissions were investigated. Important fuel properties of B10 fuel such as cetane number, viscosity, density and heat capacity were compared well with ASTM D6751 and EN 14214 specifications.While the density and viscosity of B10 fuel decreased from 0.92 kg/l to 0.83 kg/l and from 44.85 mm^2/s to 3.77 mm^2/s respectively at 26^{o}C, the heat capacity increased from 39100 kJ/kg up to 42014 kJ/kg. The produced B10 fuel has more similar properties to diesel fuel compared with raw terebinth oil.

The CO emissions decreased with biodiesel (B10 fuel) usage. Reduced CO emissions were maintained, probably, thanks to the oxygen inherently present in B10 fuel. In contrast to many researchers, the NOx emission was decreased for B10 fuel in these experiments.

Compared to the diesel fuel, 10% biodiesel blend reduced CO, CO_2 by 24% and 12%, respectively. B10 fuel reduced CO emissions by 24%, while 32% decrease in the NOx emission was experienced with the same blend. The reason for reducing three emissions (CO, CO_2 and HC) and increasing O_2 emission with biodiesel mixtures was mainly due to the presence of oxygen in their molecular structure.

Also low aromatics in the biodiesel mixtures may be an additional reason for reducing these emissions. The experimental results proved that the lower and medium percentages of B10 can partially be substituted to the diesel fuel without any modifications in diesel engine.

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