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EXPERIMENTAL INVESTIGATION OF THE USE OF WASTE MINERAL OILS WITH ORGANIC-BASED MANGANESE ADDITIVE AS A FUEL IN DIESEL ENGINES

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ABSTRACT

In the world, 45 million tons of mineral oil are consumed annually, and the vast majority of these oils are made up of petroleum-based products. Only a small part of these waste mineral oils that are produced after use are recycled while a large part is used in blending with other fuels in the energy consuming cement, lime, iron-steel and energy sectors. The thermal values of waste mineral oils are equivalent to the thermal value of fuel oil. However, for fuels such as density and viscosity, it is necessary to adapt to the system to be used for critical physical properties. It is possible to improve the physical properties of waste mineral oils by pyrolysis and cracking in conjunction with various catalysts and to use them as fuel. In this study, engine oils used in the first 10,000 km of the vehicles were used as waste mineral oil.The collected waste mineral oil is filtered with a paper filter to remove large particles. Pyrolysis or cracking has not been applied for waste mineral oil. An organic-based Mn additive is synthesized to improve the properties of the waste mineral oil. The blending of the Mn additive with the waste mineral oil at different doses (4-8-12 and 16 ppm) improved the viscosity of the waste oil and the flash point. The resulting fuel was evaluated for emission using different loads in a 5 kW capacity generator to compare with standard diesel fuel and to determine the effect of Mn addition. In the experimental study, it was observed that the emission characteristics of the fuel obtained from the waste mineral oil were worse than the diesel fuel but some improvement with the Mn addition. As a result, it appears that the use of waste mineral oils in engines due to fuel standards is unsuitable. It is also hopeful that it can be developed together with additives..

1. INTRODUCTION

In today's rapidly consuming fossil-based fuels, the development of alternative fuels for internal combustion engines is a popular research topic for both economic and environmental reasons [1-4]. There have been many studies on the production and use of biodiesel for vegetable or animal waste oils, especially for compression ignition engines. Biodiesel is important both for the assessment of waste oils and as an alternative fuel for compression ignition engines [5-8]. Especially the removal of used vegetable oils from harmless environment is an environmental issue that is carried out with great care all over the world [9-12]. However, the disposal of mineral oils (waste engine oil) used in motor vehicles is an important environmental issue. A large part of these waste engine oils are petroleum-based products, and about 1.2% of the annual oil consumption is engine oil.Especially the removal of used vegetable oils from harmless environment is an environmental issue that is carried out with great care all over the world [9-12]. However, the disposal of mineral oils (waste engine oil) used in motor vehicles is an important environmental issue. A large part of these waste engine oils are oil based products, and about 1.2% of the annual oil consumption is engine oil. Although these waste oils are of petroleum based, they are prohibited or restricted in many countries due to their use as direct fuel and/or blending with existing fuels, especially due to their environmental effects. However, the collection of these waste oils in a controlled manner is another legal requirement [13-20].

During the combustion and chemical processes that take place in the engine, the physical properties of the engine oil must not change as much as possible. However, due to the mechanical movement and high temperature of the motive, due to the substances containing carbon and sulfur which are formed by the effects of wear and burning, the engine oil also loses its characteristic with time and therefore it is necessary to renew the engine oil with certain periods. Thus waste engine oil is formed [18-20].

Due to the economic situation after the Second World War, the recycling of these waste oils has emerged to save raw materials. In the aftermath of the Second World War, refinery development in France and

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international stock exchanges, new sources for the supply of petroleum-based oils to the market were initiated and the acquisition of competitive value, that is energy saving, was promoted by considering the energy saving. Today, with the awareness of environmental hazards, many developed and developing countries have been legitimized with the idea of collecting waste mineral oil, which started with economic reasons in advance [17-20]

The European Union's "Waste Directive" 2008/98 / EC stipulates that the separate collection of waste oils at the source has a vital priority in terms of proper waste management and prevention of harm to the unfavorable after-treatment environment, analysis of life cycle according to the waste hierarchy of waste oil management it is emphasized that the most beneficial application for the environment should be given priority. According to the "Waste Management Hierarchy" stated in the directive; wastes should be reduced in source by priority order, reused, recycled as raw material, recovered as energy and finally disposed of. Life cycle analyzes provide extremely useful results in determining the most appropriate methods for environmental impacts such as recycling waste oil to base oil and using it as energy using different refining methods [21].

Only about 450 thousand tons of mineral oil consumption in Turkey in 2016 was realized. Approximately half of this consumption (200 thousand tons) is made up of engine oils used in the vehicles. It is thought that about 80% of these waste oils should be collected. However, statistics show that only 8-10% of these engine oils used can be collected as waste mineral oil. Great importance is given to the collection of waste oil in order to increase this ratio. A large proportion (70%) of the collected waste oils was obtained from the vehicle authorized services. The average 16 thousand tons of waste oil is collected each year in Turkey under the project management of waste engine oil were collected and approximately 19 thousand tons of waste oil in 2016. Approximately 12% of the collected waste oil was refined to be raw material, 86% was used as fuel in cement, lime, iron and steel plants and 2% was disposed of as hazardous waste [22]. In the world, 45 million ton of mineral oil can be collected and only 8% of these collected oils can be recycled. Although regenerated oil is obtained by recovering waste oil after chemical or physical (mechanical) regeneration, these methods are often very time consuming and costly [20, 23].

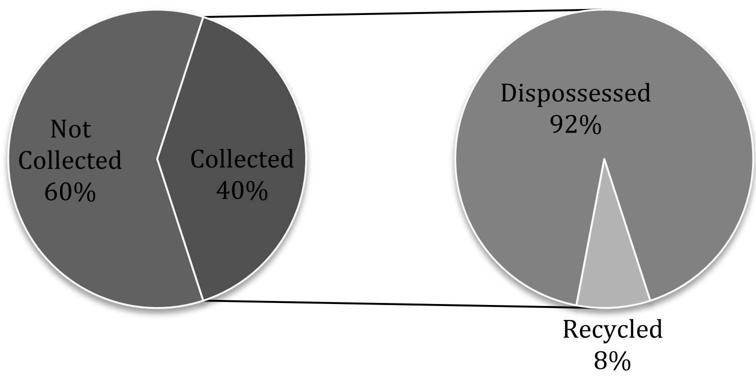

Figure 1. Waste oil recycling

There is no obstacle to the use of waste oil as fuel when environmental restrictions are adhered to. Depending on the conditions of use, waste engine oils contain metal and derivatives and some ash. Such materials can be removed from waste oil by various filter methods. For the use of waste oils as direct fuel only the application of the filter process may not be sufficient. Depending on the use of waste oil as fuel, some of the thermal and physical properties of the oil should be made compatible with the system to be used. While work on the use of waste oil as a direct fuel is ongoing, it is also possible to mix it with existing fuels [20].

There are many studies on the use of waste engine oils as fuel in engines [24-32]. When these studies are examined it is seen that gasoline-like or diesel-like fuels are obtained from waste engine oils by pyrolytic distillation in general [24-27]. Arpa et al. studied pyrolytic distillation and investigated the thermal and physical properties of fuels after mixing the sodium carbonate, zeolite and lime additives (catalysts) in filtered waste oil at certain percentages [24]. Balat, in his work, blended perlite and wood ash in filtered oil for pyrolytic distillation. Balat mentioned that waste engine oils could be used in gasoline engines as an alternative fuel [25].

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Balat et al. have stated that by mixing pyrolysis with filtered wood waste ash, alternative gasoline or diesel fuel can be obtained [26]. Demirbaş mentions that waste engine oils can produce olefin-rich oils at elevated temperatures and that these oils can be obtained with gasoline-like fuel with 96 octane number of prolyl in the presence of aluminum catalyst [27]. Kannan et al. note that zeolite can be reformed in the presence of a catalyst to convert waste engine oils into a fuel suitable for diesel engines. For this, the physical and thermal properties of the oil obtained after reforming are compared with those of diesel fuel. The resulting oil is said to be usable in diesel engines [28]. Maceiras et al. have been converted to fuels by pyrolytic distillation in the presence of sodium hydroxide and sodium carbonate catalyst, which can be used in waste engine oil diesel engines. With this study, it has been stated that conversion of waste engine oil to diesel fuel can be achieved by pyrolytic distillation in the presence of 2% sodium carbonate [29]. In their study, Prabakaran and colleagues examined the physical and thermal properties of waste engine oil reformed in acetic acid and clay compartments by diesel fuel at various ratios. The resulting mixture was tested in a fuel diesel engine and was reported to reduce specific fuel consumption, nitrogen-oxide and HC emissions [30]. Zandi et al. obtained catalytic conversion of waste engine oil to diesel engines in the presence of the nano-CeO_2 / SiO_2 catalyst synthesized by different analytical methods and examined the physical and thermal properties of the fuel [31]. Aburas et al. describe the use of pyrolysis and cracking methods to convert waste engine oils to reusable products such as gasoline, diesel and fuel oil. In the study conducted, calcium oxide was used as an additive in various proportions [32].

When assessed in terms of energy intensity, petroleum-based waste oils have a great potential. However, it is also known that direct use of waste oils is very disadvantageous when evaluated environmentally. Because of the uncontrolled use of these waste oils, loss of life and property can be experienced as well as harming the country's economy and also causing great environmental problems [18-20]. Similarly, waste vegetable and animal fats can be obtained through a series of processes for use in internal combustion engines to obtain fuel oil (biodiesel). However, fuel properties can be improved with organic based additives used with fuels derived from waste vegetable and animal oils [33-51]. Commonly used synthetic additives are generally selected from the group consisting of barium [33], aluminum and its oxides [51], carbon [34], turpentine [35], manganese and oxides [36, 37, 43, 46, 47], iron [39], cerium [40, 41, 45], Magnesium and its oxides [42-44, 46, 50], platinum [45], nickel [47], molybdenum and its oxides [48], calcium, copper and oxides [43]. Similar to this situation, it is thought that similar treatments can be done on waste engine oil and it can be used as safe fuel by developing various additives.

In this study, it is aimed to investigate engine performance and emission of the waste engine oil as a fuel in diesel engines after a series of physical filtration and mixing with organic based manganese (Mn) additive.

2. MATERIALS AND METHOD

Waste Mineral Engine Oil

Waste mineral oils are generally divided into two groups as waste mineral engine (or automotive) oil and waste mineral industrial oil. Waste metal engine oils are considered different from industrial waste oils due to the usage conditions. Waste motor oils are generally derived from passenger cars and commercial vehicles. Waste motor oils are called black waste oil due to their color. Waste oils used in machines that are not combustible are called clean waste oil [20-23].

Mineral oils, one of the products obtained by processing crude oil in refineries, are again subjected to special treatment to obtain base oils, which are raw materials of mineral oils. These oils are classified according to their viscosities. Although mineral oils are petroleum-based products, they are obtained by mixing various viscous base oils with various additives, which are selected according to the properties expected from the product. It is possible to find mineral oils in various brands and specifications in the sector [20-23]. These oils are produced from different base oils and different chemistries. The base oils used can be aliphatic or aromatic. Mineral oils are collected as waste oil after use. These collected oils have different characteristic oils that are manufactured from different base materials, manufactured with different additives and worked under different conditions. Such sorting of waste oils is a difficult and costly task. For this reason, waste metallic engine oils are generally recycled by being characterized as a single feature [52-56]

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The waste oil used in this study was waste lubricant after the first 10000 km of the vehicles which were called as the first run-off oil. The run-off oil does not carry a different oil feature. Since the purpose of the work is the availability of waste mineral oils as direct fuel, filtration with only paper filter has been done so that the waste mineral oils can be cleaned after collecting the large particles.

Preparation of the Fuel with Organic Based Mn Additive

The method of synthesizing organic based additives has been described in detail in earlier work [37, 42-44, 46-48]. In a one liter reactor equipped with a reflux condenser, abietic acid (resin acid) and manganese dioxide (MnO_2) were introduced into the reaction mixture at 150°C in an oiled medium with the aid of a magnetic stirrer, and an organic-based manganese compound was synthesized. The mass ratio for MnO_2, abietic acid and oil was 1: 2.9: 6.5. The additive, which was converted into solution with the alcohol and hydrocarbon compounds, was mechanically drained at different concentrations and dosed to the mineral oil (4, 8, 12 and 16 ppm) for one day. Ethanol was added to ensure the solubility of the mixture. For the determination of the kinematic viscosity of the obtained fuel, the Engler viscometry was determined by the Clevland open cup method for flash point determination.

3. EXPERIMENTAL SETUP

A diesel generator with a maximum power of 5 kW was used to determine the effects on the diesel engine of the fuel prepared by dosing the Mn-based additive to the waste mineral oil. The diesel engine used in the generator can generate 6.4 kW of power at 3000 rpm [57]. The characteristics of the diesel generator are as follows.

Table 1. General characteristics of the generator used in the experiment [57]

Generator model	P-7500 DE
Engine model	186-FAE
Alternator type	Monophase
Max alternatorpower	5 kW
Contunious alternator power	4.5 kW
Alternator speed	3000 rpm (50 Hz)
Alternator mechanical efficiency	0.8
Mean fuel consumption	2.23 l/h
Max engine power	6.4 kW@3000 rpm
Contunions engine power	5.7 kW@3000 rpm
Cooling System	Air cooled
Intake system	Natural aspirated
Stroke x Diameter	86mm x 72 mm
Compression ratio	19:1
Stroke Volume	418 cm^3

The generator used in the experiments is operating at a fixed 3000 rpm motor speed and this speed is regulated according to the alternator load [57]. However, when the test fuel is changed, there is some change in this constant speed and the generator is having difficulty regulating this speed. Small adjustments have to be made for this. In the experiments, 6 resistive loads were formed with electrical resistances in the range of 0.75-4.5 kW (Figure 2). Effective motor power was determined by proportion of this reactive load alternator to fixed mechanical efficiency. The generator is known to have a mechanical efficiency of 80% [57].

$$P_{e,exp} = \frac{P_{res}}{\eta_{m,alt.}} \quad (1)$$

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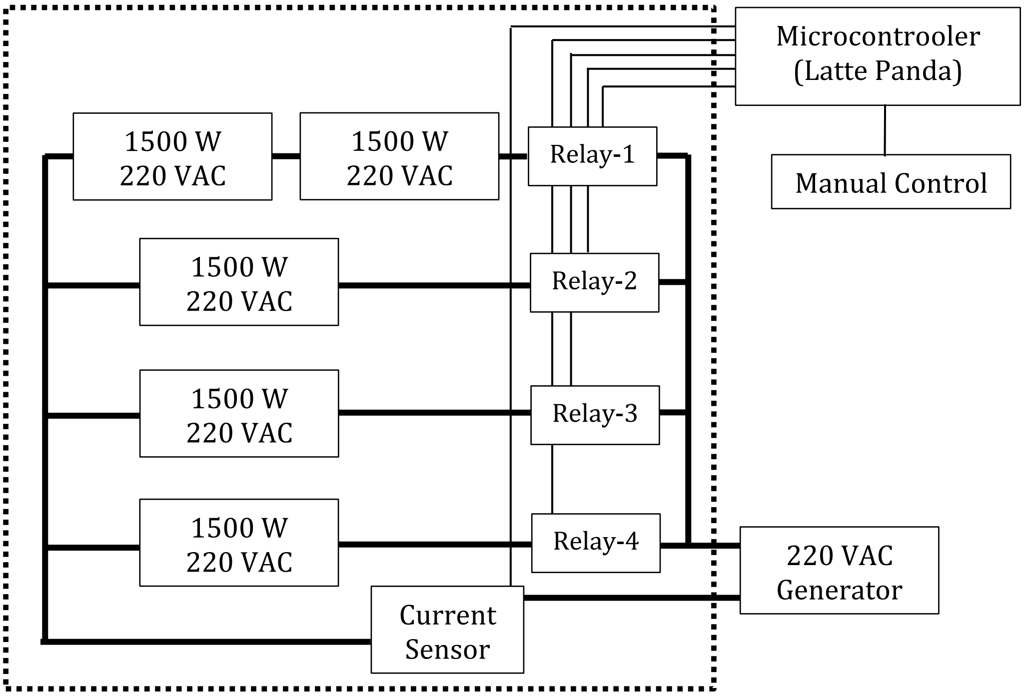

Figure 2. Resistive load cycle

The external environment conditions in which the engine test is performed affect the engine performance. In order to be able to compare the results of engine tests on different conditions in a healthy way, they have to be converted into standard conditions. The correction coefficient for the diesel engines according to the standard values measured can be calculated as follows [58-59].

$$P_e = k.P_{e,exp} \tag{2}$$

$$k = \left(\frac{101.3}{P_{amb.(kPa)}}\right)^{0.65} \left(\frac{T_{exp.(K)}}{293}\right)^{0.5} \tag{3}$$

The test environment conditions were measured with the TFA 35.1083 digital portable weather station. Experiments were carried out at a temperature of 22°C (295 K) and a pressure of 91 kPa. Throughout the experiments these conditions have not changed. Accordingly, the correction coefficient is calculated as k=1.075. In the experiments, volumetric fuel measurements were made. The time of use of the 20 ml fuel with the graduated container was measured and the hourly mass fuel consumption was then calculated.

$$\dot{m}_f\,[\mathrm{g/h}] = \frac{72.\rho_f\,[\mathrm{g/l}]}{t\,[\mathrm{s}]} \tag{4}$$

ρ_f is the fuel density and the fuel densities used in the experiment are measured by a 10.350 ml calibrated density bottle (pycnometer) at 20°C. The densities of the fuels used in the experiments were calculated as 0.810 g/L and 0.851 g/L for diesel fuel and additive waste mineral oil, respectively. Specific fuel consumption is calculated by the ratio of fuel consumption to engine power. In order to operate the generator constantly at a constant speed, a rotary encoder is installed at the rear of the diesel engine and small adjustments are made to keep the engine speed constantly under control. The oil temperature is used as reference for the engine's stable operating conditions, since the oil temperature in air-cooled engines is considered as a more sensitive measuring point than the body temperature.

It is expected that the oil temperature will be stabilized by waiting about 25 minutes after starting the generator and it is expected for other loads as well. The oil temperature measurement was made using the universal temperature indicator with the EMKO PT-100 temperature sensor installed instead of the oil filling plug. In the

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experiments, emission measurement is limited by particle measurement and smoke density. The aim of the emission measurement here is to compare the contribution prepared for the waste oil in terms of the amount of particulate and smoke density which is an emission criterion for diesel engines. For this reason, no measurement with gas analyzer was needed. The Mobydic 5100 emission instrument used in the experiments can measure the smoke intensity at 0-100% (or 1-20 m^{-1}) and the amount of particles at 0-1000 mg/m^3. In general, the schematic representation of the experimental setup is as shown in Fig 3.

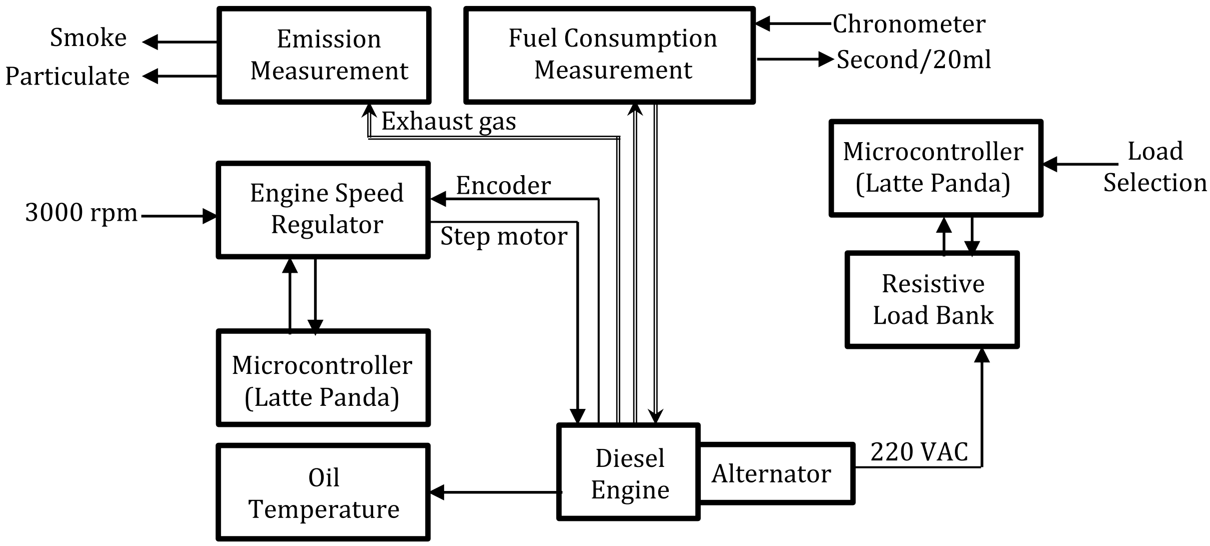

Figure3. Experimental setup

In this study, the change of the properties of waste mineral oil was investigated primarily by dosing of the additive. The experimental set was then used as standard diesel fuel, unmixed waste mineral oil and standart diesel engine fuel of 16 ppm dosed waste mineral oil with organic based Mn additive. The results of the experiments were used to determine the effect of the additive and the use of the waste mineral oil as fuel in the diesel engines by obtaining emission and fuel consumption values.

4. RESULTS AND DISCUSSION

Some Properties of the Obtained Test Fuel

The change in kinematic viscosity and flashpoint values of the organic based Mn additive dosed waste mineral oil with respect to the amount of additive substance in the laboratory is as follows (Fig. 4 and Fig. 5).

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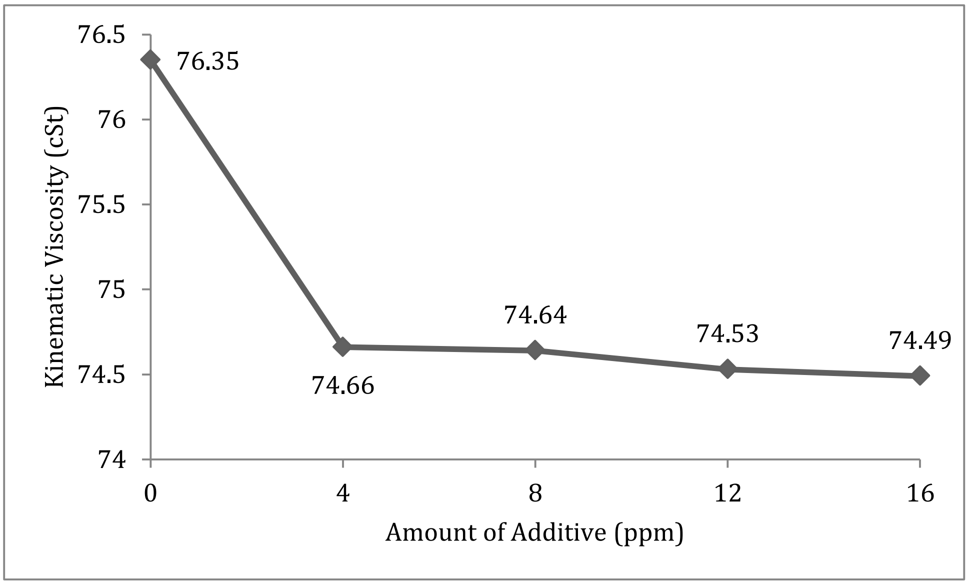

Figure4. Effect of organic Mn additive on kinematic viscosity

High pumping pressure is also needed with high viscosity value [60-61]. The standard kinetic viscosity of a standard diesel fuel at 40°C is in the range of 1.9 to 4.5 cSt [61-62]. According to the results obtained, although the additive is seen to have a kinematic viscosity lowering effect, it is far from standard values at present. However, the effect of Mn addition on the kinematic viscosity after a certain dose is very small. Waste motor oil is only filtered and cleaned additive is added. If a process for reducing viscosity is performed independently of the additive for waste engine oil, the kinematic viscosity of the fuel obtained with the additive material will be approximated to the standards.

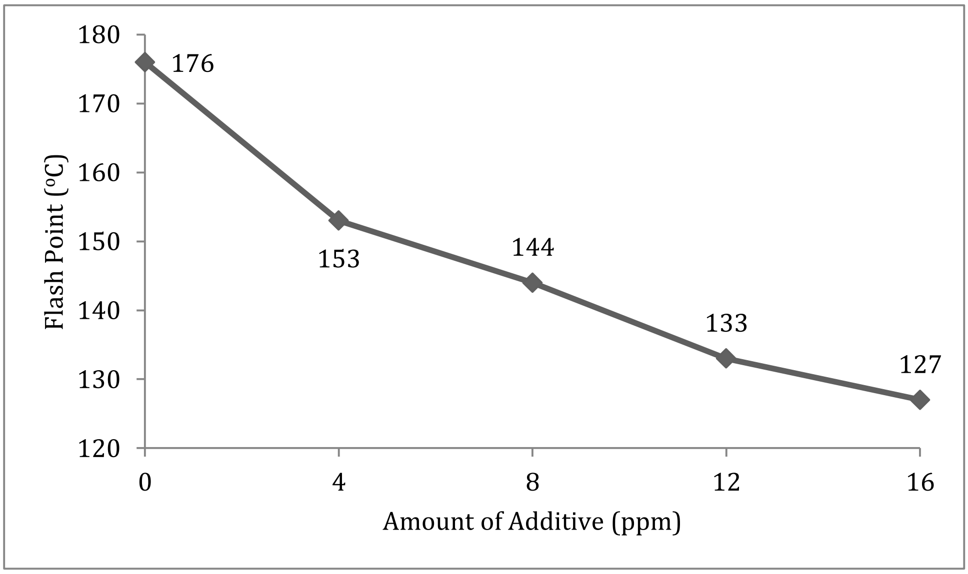

Figure 5. Effect of organic Mn additive on flash point

The flash point of diesel fuels is about 52 ° C [60]. The low self-ignition temperature of the diesel fuel flash point is desirable. When the effect of manganese additive on the ignition point of waste motor oil is examined, it is seen that the additive is a reducing effect of the flash point.

The results from these laboratory tests were compared according to the EN 590 standard and found to be close to the diesel fuel standards with the additive [63]. As a result of all these experiments it was decided to use 16

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ppm organic Mn additive dosed waste oil in the experiments. After this step, engine performance and emissions were compared comparatively using standard engine, unleaded waste lubricant, and additive waste mineral oil in the engine test set.

Effect of Mn Additive on Stable Working Temperature

In internal combustion engines, depending on the engine load, it works at the average constant temperature with the effect of the cooling system. In air-cooled engines there are air fins for cooling and a fan that provides air flow to these air fins. The generator used in the experiments has cooling fan blades on the flywheel. The flow rate of the cooling air is constant as the engine is operated at constant speed. In the experiments, the oil temperature was taken as reference for reaching the stable working temperature of the engine. After a short time (approx. 25 minutes), the oil temperature becomes constant (Figure 6).

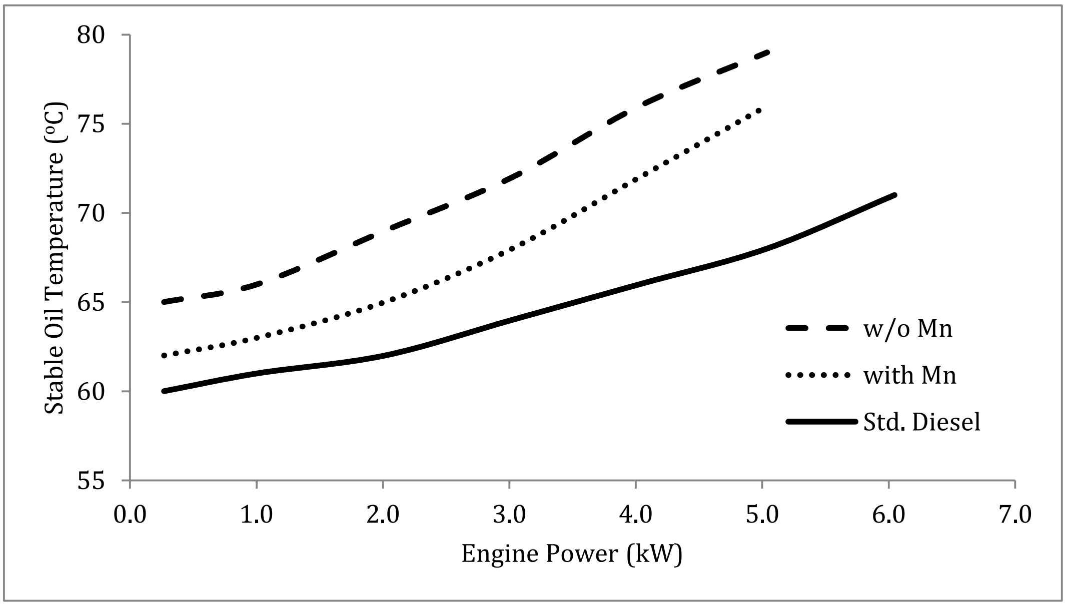

Figure 6. Effect of the organic Mn additive on the working temperature

With Mn addition, the stability working temperature decreased by about 5%. The Mn additive has brought the stable working temperature of the waste mineral oil closer to the fuel of the engine. The reduction of stable working temperature can be shown as the improvement of atomization by the effect of reduction of viscosity together with the contribution of Mn additive and accordingly the improvement of the burn. Decreasing fuel consumption with reduced stable working temperature is expected.

Effect of Mn Additive on Fuel Consumption

Along with the use of waste mineral oil instead of diesel fuel, there was some decrease in engine speed. The fuel pump has been calibrated to regulate the engine speed again. For this reason, a slight increase in fuel consumption compared to diesel fuel has come to the fore. However, with the Mn additive, it seems that fuel consumption has decreased somewhat. Along with the Mn additive, there are marked differences in the properties of the fuel such as viscosity and flash point. The effect of these differences is observed in the fuel consumption and specific fuel consumption as well as in the stabilized temperature (Figure 7 and Figure 8).

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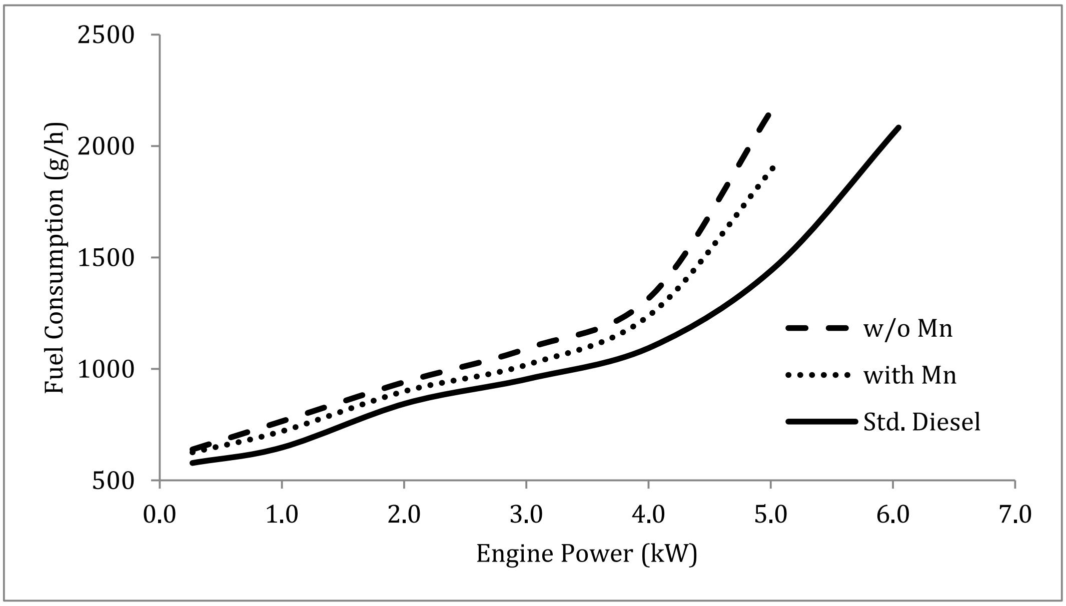

Figure7. Effect of organic Mn additive on fuel consumption

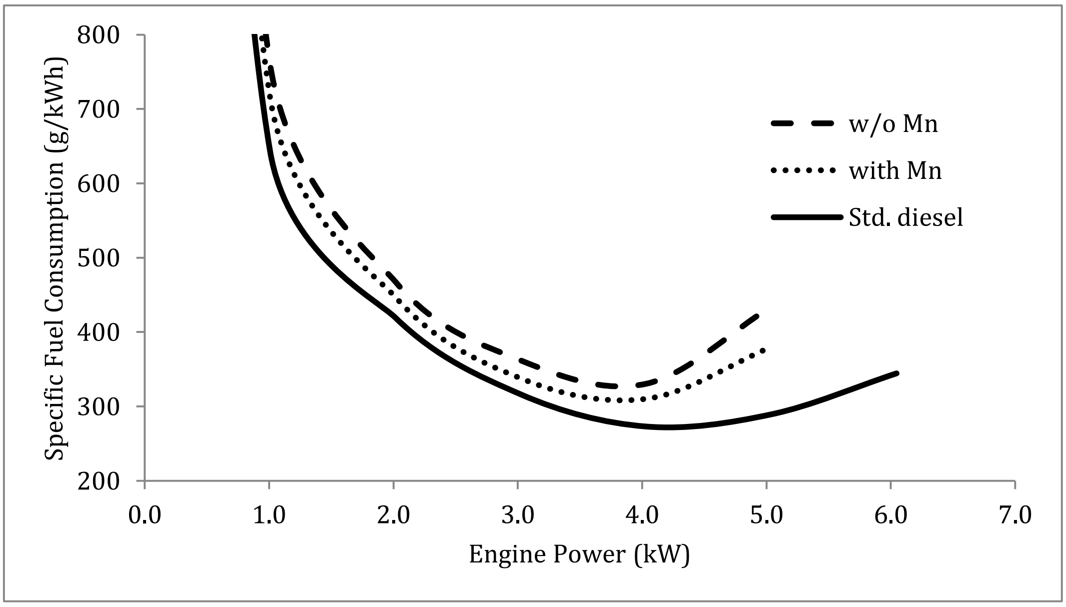

Figure8. Effect of organic Mn additive on specific fuel consumption

Along with the Mn additive, less fuel is consumed for the same engine load. Given the decrease in stable working temperature, it has been shown to decrease in lost heat. Specific fuel consumption, which is another expression of thermal efficiency, has decreased with the Mn additive for the same engine power.

Effect of Mn Additive on Exhaust Emissions

In diesel engines, emission measurement can be done in detail with gas analyzer as well as with diesel smoke tester. However, in this study, a visible darkness was observed in the exhaust smoke with the burning of the waste oil. In diesel engines, the color of the exhaust gas indicates that the combustion is good or bad, and therefore, only the amount of smoke and particulate matter is measured in this study instead of the detailed gas analysis.

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Smoke density is defined as the percentage of non-transparent particles in the exhaust gas that reduce the intensity of the light they pass through when crossing the section [64-65]. However, another indicator of smoke density is the light absorption coefficient. Smoke density and light absorption coefficient are two emission indices with the same tendency. Light absorption coefficient is limited to 2.5-3 1 / m in diesel engines. These limits also apply to generator motors [65-67] (Figure 9).

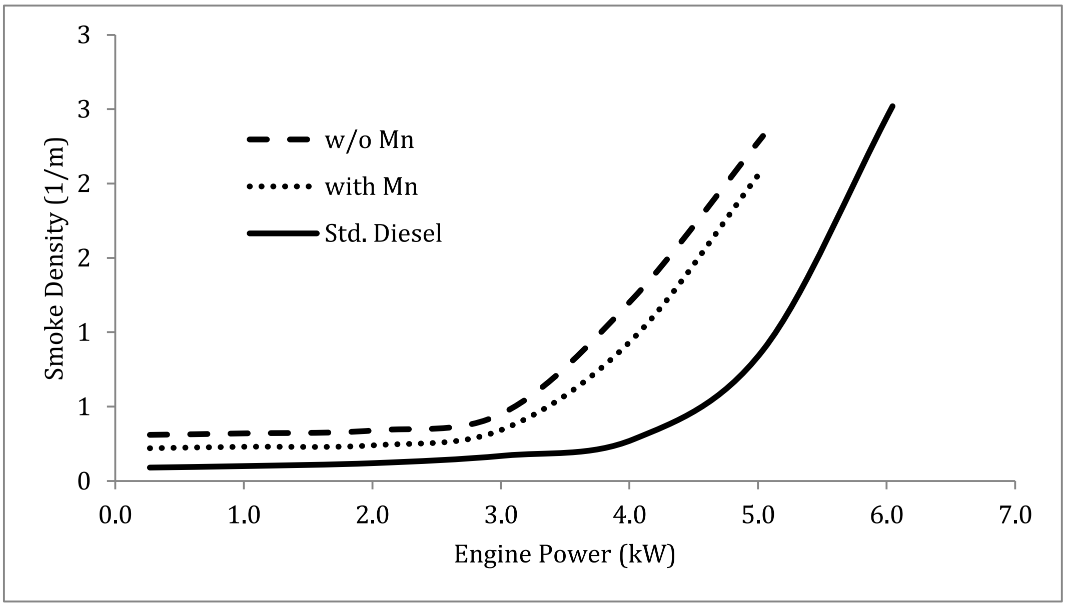

Figure9. Effect of organic Mn additive on light absorption coefficient

The light absorption coefficient in experiments with diesel fuel at high engine loads is at normal levels. However, when waste mineral oil is used, it is not possible to measure because of the tendency of the engine to stop in high engine loads and excessive smoke. Along with the Mn additive, there is a decrease in the light absorption coefficient for the same motor load. When the amounts of the particulate matter are compared, it is seen that the Mn addition is also the effect of reducing the amount of the particulate matter (Figure 10).

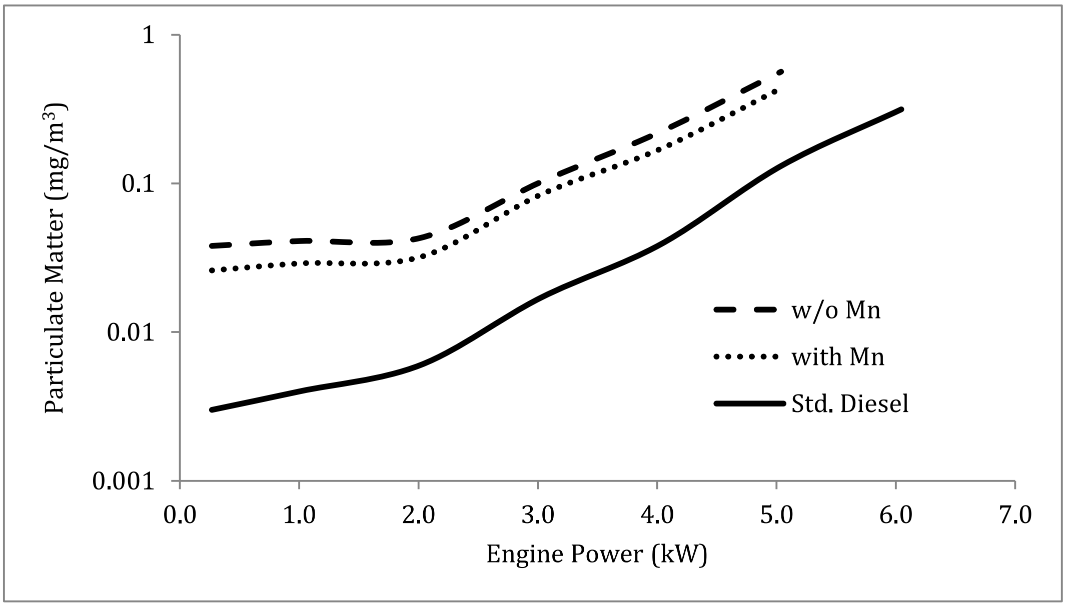

Figure10. Effect of organic Mn additive on the amount of particulate matter

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5. CONCLUSION

The effects of organic-based metal additives on engine performance and emissions have been observed in previous studies for biodiesel fuels derived from motor and different vegetable and animal oils in previous studies [34-42]. However, studies on waste mineral oils have focused on the recycling of waste mineral oils after different chemical and mechanical processes [24-32]. It is known that the organic based metal additives synthesized from metal oxides are the effect of improving the properties of fuels used in diesel engines. In this study, the availability of waste mineral oils as a direct fuel in diesel engines was investigated firstly and then the improvementability of organic Mn additive material was investigated experimentally. As a result, when evaluated in terms of engine performance and emissions, it appears that waste mineral oils are not directly usable in diesel engines, especially in systems operating under constant and stable conditions, such as generators. However, with the organic-based Mn addition, the fuel characteristics of the waste mineral oil are closer to the engine. In conjunction with this study, it has been possible, in part, that the organic-based Mn additive can be used in diesel engines. Economically, both waste oil and additives do not cost much to be tested. An economic value can be obtained with the development of this study. As a result of the work being done, it has been understood that the critical fuel properties such as viscosity should be improved by passing the waste engine oils through different processes instead of using them directly. In subsequent work, additives of different types of metal oxides can be tested by adjusting the viscosity of the waste engine oil according to the standards. However, a more detailed examination can be made by performing internal cylinder pressure measurement and combustion and heat emission analysis.

6. CONFLICTS OF INTEREST

The authors declare that they have no conflicts of interest regarding the publication of this paper.

7. ACKNOWLEDGEMENT

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