

1 Article

2 Experimental Investigation of the Use of Waste 3 Mineral Oils as a Fuel with Organic-based Mn 4 Additive

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11

12 **Abstract:** The heat values of waste mineral oils are equal to the heat value of the fuel oil. However,
13 heat value alone is not sufficient for the use of waste mineral oils. as fuel. However, the critical
14 physical properties of fuels such as density and viscosity need to be adapted to the system in order
15 to be used. In this study, the engine oils used in the first 10,000 km of the vehicles were used as
16 waste mineral oil. An organic-based Mn additive was synthesized to improve the properties of the
17 waste mineral oil. It was observed that mixing the Mn additive with the waste mineral oil at different
18 doses (4, 8, 12 and 16 ppm) improves the viscosity of the waste oil and the flash point. The resulting
19 fuel was evaluated for emission using different loads in a 5 kW capacity generator to compare the
20 fuel with standard diesel fuel and to determine the effect of Mn addition. In the experimental study,
21 it was observed that the emission characteristics of the fuel obtained from waste mineral oil were
22 worse than diesel fuel, but some improvement with Mn addition. As a result, we found that the use
23 of waste mineral oils in engines in fuel standards was not appropriate, but may be improved with
24 additives.

25 **Keywords:** waste mineral oil; Mn additive; engine performance; emission

26

27 1. Introduction

28 Development of alternative fuels instead of rapidly consuming fossil-based fuels, especially for
29 internal combustion engines, is an important and critical issue for humanity, both for economic and
30 environmental reasons [1]. It is possible to find many studies on the use of vegetable or animal waste
31 oils instead of diesel fuel by esterification. These fuels, which are called biodiesel fuels, are very
32 important for the use of waste oil as an alternative fuel [2-3]. Nowadays, the disposal of used or waste
33 vegetable oils is an environmental and legal necessity, and the use of these wastes as fuel seems to be
34 an important energy potential [4-5]. The use of oil produced from the waste tire as fuel and the
35 production of synthetic diesel fuel from renewable sources are at least as popular research topics as
36 biodiesel [6-10]. The disposal of waste mineral oils is an important question, just like the disposal of
37 vegetable oils [11]. The heat values of waste mineral oils are equal to the heat value of the fuel oil (42-
38 44MJ/kg) [12]. A large part of these waste engine oils are petroleum-based products, and
39 approximately 1.2% of annual petroleum is consumed of engine oil. Although these waste oils are
40 petroleum-based, their blending with direct fuels and / or existing fuels is prohibited or restricted in
41 many countries, especially due to their environmental impact. However, the collection of these waste
42 oils in a controlled manner is another legal requirement [13].

43 During combustion and chemical processing, the physical properties of engine oil must not
44 change as much as possible. However, due to mechanical movement, a high temperature, and

45 particulate matter, engine oil gradually loses its properties, and engine oil therefore needs to be
46 replaced in a determined period. Thus, waste oil is formed [14]. Due to the economic situation after
47 the Second World War, the recycling of these waste oils emerged in order to save raw materials. In
48 the aftermath of the Second World War, as a result of refinery development in France and
49 international stock exchanges, new sources for the supply of petroleum-based oils to the market were
50 introduced and the acquisition of competitive value, that is, energy saving, was promoted by
51 considering energy saving [15]. Today, with the awareness of environmental hazards, many
52 developed and developing countries have been legitimized with the idea of collecting waste mineral
53 oil, which started with economic reasons in advance [14].

54 According to the European Union's "Waste Directive", it is foreseen that the separate collection
55 of waste oils has a vital importance in terms of proper waste management and prevention of harm
56 from unsuitable treatment environment judging by, analyses according to the life cycle. According
57 to the "Waste Management Hierarchy" specified in the Directive; it is emphasized that the most
58 beneficial application for the environment should be given priority. Waste must be reduced, recycled,
59 recycled as raw material, recovered as energy, and ultimately disposed of at the source according to
60 priority order [16].

61 There is no obstacle to the use of waste oil as fuel when environmental restrictions are adhered
62 to. Depending on the conditions of use, waste engine oils contain metal and derivatives and some
63 ash. Such materials can be removed from waste oil by various filtration methods. However the use
64 of the waste oils as direct fuel, only the application of the filter process may not be sufficient.
65 Depending on the use of waste oil as fuel, some of the physical properties of the oil should be made
66 compatible with the system to be used. While work on the use of waste oil as a direct fuel is ongoing,
67 it is also possible to mix it with existing fuels [17].

68 There are many studies on the use of waste engine oils as fuel in engines. When these studies
69 are examined it is observed that gasoline-like or diesel-like fuels are obtained from waste engine oils
70 by pyrolytic distillation in general. Arpa et al. studied pyrolytic distillation and investigated the
71 thermal and physical properties of fuels after mixing the sodium carbonate, zeolite and lime additives
72 (catalysts) in filtered waste oil at certain percentages [15]. Balat, in his work, blended perlite and wood
73 ash in filtered oil for pyrolytic distillation. Balat mentioned that waste engine oils could be used in
74 gasoline engines as an alternative fuel [18]. Balat et al. have stated that by mixing pyrolysis with
75 filtered wood waste ash, alternative gasoline or diesel fuel can be obtained [19]. Demirbaş mentions
76 that waste engine oils can produce olefin-rich oils at elevated temperatures and that these oils can be
77 obtained with gasoline-like fuel with 96 octane number of prolyl in the presence of an aluminum
78 catalyst [20]. Kannan et al. note that zeolite can be reformed in the presence of a catalyst to convert
79 waste engine oils into a fuel that is suitable for diesel engines. For this, the physical and thermal
80 properties of the oil obtained after reforming are compared with those of diesel fuel. The resulting oil
81 is said to be usable in diesel engines [21]. Maceiras et al. have converted fuels by pyrolytic distillation
82 in the presence of sodium hydroxide and sodium carbonate catalyst, which can be used in waste
83 engine oil diesel engines. With this study, it has been found that the conversion of waste engine oil
84 to diesel fuel can be achieved by pyrolytic distillation in the presence of 2% sodium carbonate [22].
85 In their study, Prabakaran and colleagues examined the physical and thermal properties of waste
86 engine oil reformed in acetic acid and clay compartments by diesel fuel at various ratios. The resulting
87 mixture was tested in a fuel diesel engine and was reported to reduce specific fuel consumption,
88 nitrogen-oxide and hydrocarbon (HC) emissions [23]. Zandi et al. studied the catalytic conversion of
89 waste engine oil to diesel engines in the presence of the nano-CeO₂/SiO₂ catalyst synthesized by
90 different analytical methods and examined the physical and thermal properties of the fuel [24].
91 Aburas et al. describe the use of pyrolysis and cracking methods to convert waste engine oils to
92 reusable products such as gasoline, diesel and fuel oil. In the study conducted, calcium oxide was
93 used as an additive in various proportions [25].

94 Unlike the studies in the literature, we investigated the possibility of using diesel fuel as a fuel
95 mixed with organic-based Mn addition only after the mechanical filtration process without any heat
96 treatment in waste mineral oil in this study. We aimed to investigate the engine performance and

97 emissions of waste engine oil as a fuel in diesel engines by mixing it with a series of physical filtration
98 and organic-based Mn additives.

99 2. Materials and Method

100 2.1. Waste Mineral Oil

101 Waste mineral oils are generally divided into two groups as the waste mineral engine (or
102 automotive) oil and waste mineral industrial oil. Waste metal engine oils are considered different
103 from industrial waste oils due to the usage conditions. The waste mineral engine oils operate under
104 more severe conditions such as high temperature, high pressure, and combustion. Waste engine oils
105 are called black waste oil due to their color. Waste oils used in machines that are not combustible are
106 called clean waste oil [26].

107 Mineral oils are collected as the waste oil after use. These collected oils have different
108 characteristic oils that are manufactured from different base materials, manufactured with different
109 additives and worked under different conditions [27]. Such sorting of waste oils is a difficult and
110 costly task. For this reason, waste metallic engine oils are generally recycled by being characterized
111 as a single feature [28].

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

117 2.2. Organic Based Mn Additive and Fuel

118 The method of synthesizing organic based additives has been described in detail in earlier work
119 [23-29]. For the synthesis of the organic-based Mn additive, in a one liter reactor equipped with a
120 reflux condenser, abietic acid (resin acid) and manganese dioxide (MnO_2) were introduced into the
121 reaction mixture at 150°C in an oiled medium with the aid of a magnetic stirrer, and an organic-based
122 manganese compound was synthesized. The mass ratio for MnO_2 , abietic acid and oil were 1: 2.9:
123 6.5. The additive, which was converted into solution with the alcohol and hydrocarbon compounds,
124 was mechanically drained at different concentrations and dosed with the mineral oil (4, 8, 12 and 16
125 ppm) for one day. Ethanol was added to ensure the solubility of the mixture. For the determination
126 of the kinematic viscosity of the obtained fuel, the Engler viscometry was determined by the Cleveland
127 open cup method for flash point determination.

128 2.3. Experimental Setup

129 A diesel generator with a maximum power of 5 kW was used to determine the effects on the
130 diesel engine of the fuel prepared by dosing the Mn-based additive to the waste mineral oil. The
131 diesel engine used in the generator can generate 6.4 kW of power at 3000 rpm [36]. The characteristics
132 of the diesel generator are as follows (Table 1).

133 **Table 1.** General characteristics of the generator used in the experiment [36]

Specification	Explanation
Generator model	P-7500 DE
Engine model	186-FAE
Alternator type	Monophase
Max alternator power	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

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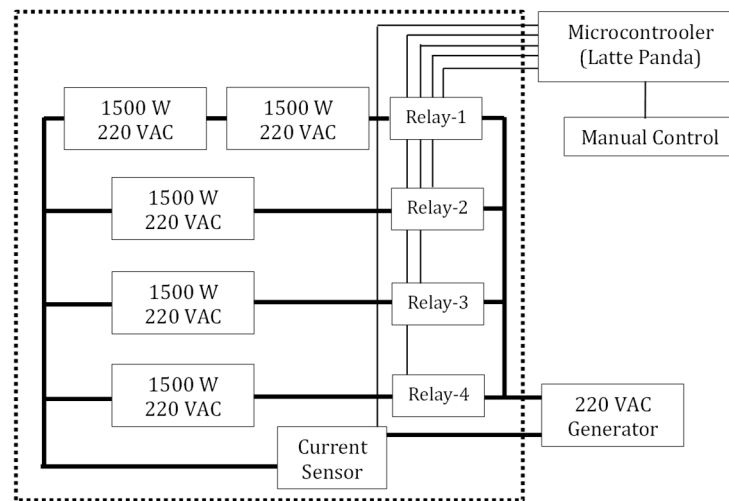
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The generator used in the experiments was operated at a fixed 3000 rpm engine speed, and this was regulated according to the alternator load. However, when the test fuel was changed, there was some change in this constant speed and the generator had difficulties regulating this speed. Small adjustments have to be made for this. In the experiments, six resistive loads were formed with electrical resistances in the range of 0.75-4.5 kW (Figure 1).



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Figure 1. Resistive load cycle

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The heater at 1500 W rated current drew approximately 6.8A current at 220V mains voltage and the resistance value of this heater is approximately 32 ohms. When two 1500W nominal heaters were connected in series, the resistance in the circuit doubled and the current drawn was reduced by half. In this case, the total power of these two heaters connected in series is 750W. When two 1500W nominal heaters are connected in parallel, the resistance in the circuit is reduced by half and the total current is drawn up doubled. In this case, the total power of these two heaters connected in parallel will be 3000W. Similar calculations can be made for other situations. The power values here are governed by whether the relays connected to the microprocessor card were open or closed. For example, power 750W when relay 1 was on, power 1500W relay 1 when relay 2 is on, and power 2250W when relay 2 is on. Effective engine power was determined by the proportion of this reactive load alternator compared to the fixed mechanical efficiency. The generator was known to have a mechanical efficiency of 80%.

$$P_{e,corrected} = k \cdot P_{e,exp} \quad (1)$$

$$k = \left(\frac{101.3}{P_{amb.(kPa)}} \right)^{0.65} \left(\frac{T_{exp..(K)}}{293} \right)^{0.5} \quad (2)$$

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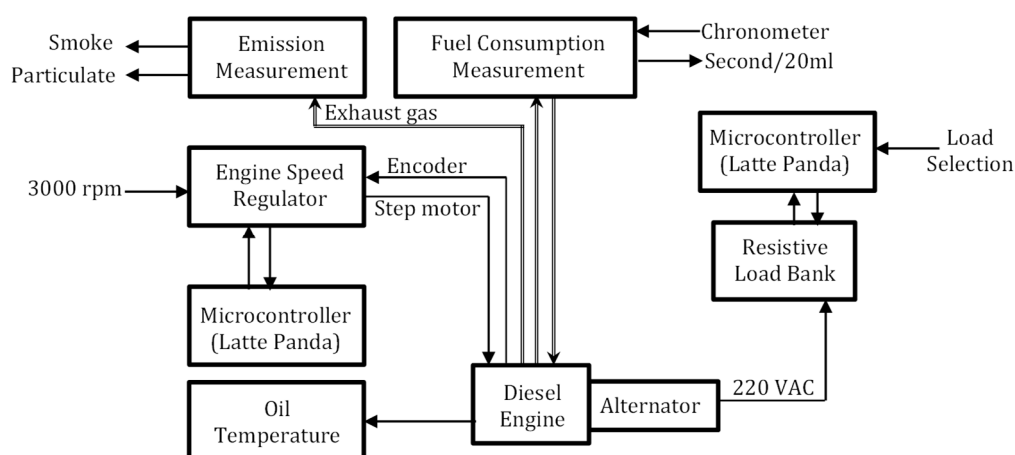
Experiments were carried out at a temperature of 22°C (295 K) and a pressure of 91 kPa. Throughout the experiments, these conditions were not changed. Accordingly, the correction

156 coefficient was calculated as $k=1.075$. In the experiments, volumetric fuel measurements were made.
 157 The time of use of the 20 ml fuel with the graduated container was measured and the hourly mass
 158 fuel consumption was then calculated.

$$\dot{m}_f \text{ [g/h]} = \frac{72 \cdot \rho_f \text{ [g/l]}}{t \text{ [s]}} \quad (3)$$

159 ρ_f is the fuel density and the fuel densities used in the experiment were measured by a 10.350
 160 ml calibrated density bottle (pycnometer) at 20°C. The densities of the fuels used in the experiments
 161 were calculated as 0.810 g/L and 0.851 g/L for the diesel fuel and additive waste mineral oil,
 162 respectively. The density of waste engine oil is 5% higher than that of the diesel fuel. The density of
 163 biodiesel is in the range of 860-900 g/L and the density of the waste engine oil is lower than the density
 164 of the biodiesel. The density affects fuel consumption, and as the hydrocarbon chain grows, the
 165 density decreases and as the number of double bonds increases, the density increases. Specific fuel
 166 consumption was calculated by the ratio of fuel consumption to engine power. In order to operate
 167 the generator at a constant speed, a rotary encoder was installed at the rear of the diesel engine, and
 168 small adjustments were made to maintain the engine speed constantly under control. The oil
 169 temperature was used as a reference for the engine's stable operating conditions since the oil
 170 temperature in air-cooled engines was considered as a more sensitive measuring point than the body
 171 temperature.

172 It was expected that the oil temperature would be stabilized by waiting approximately 25
 173 minutes after starting the generator, and this was expected for other loads as well. The oil
 174 temperature measurement was made using the universal temperature indicator with the PT-100
 175 temperature sensor installed instead of the oil filling plug. In the experiments, emission measurement
 176 was limited by particle measurement and smoke density. The amount of particulate matter and
 177 smoke concentration values used as emission indicators of diesel engines was found to be sufficient
 178 since the intended use of the engine was limited to the use of waste engine oils in diesel engines. The
 179 aim of the emission measurement here was to compare the contribution prepared for the waste oil in
 180 terms of the number of particulate and smoke density which is an emission criterion for diesel
 181 engines. For this reason, no measurement with gas analyzer was needed. The emission instrument
 182 used in the experiments could measure the smoke intensity at 0-100% (or 1-20 m^{-1}) and the amount
 183 of particles at 0-1000 mg/m^3 . The schematic representation of the experimental setup is as shown in
 184 Figure 2.
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Figure 2. Experimental setup

188 The resistive load bank and microcontroller, shown in figure 1 and figure 2 in detail. The
 189 resistive load bank was directly connected to the electrical power socket of the generator. To operate
 190 the engine at a constant speed of 3000 rpm, a simple step motor was placed on the fuel setting
 191 mechanism and the position of the step motor is changed according to the engine speed value that

192 was read from the encoder. For any engine load, a period of time was required before the engine
193 speed could be stabilized.

194 In this study, the change in the properties of the waste mineral oil was investigated primarily by
195 the dosing of the additive. In the experiments, standard diesel fuel, waste engine oil without Mn
196 additive and waste engine oil with Mn additive are used as fuel. The results of the experiments were
197 used to determine the effect of the additive and the use of the waste mineral oil as fuel in the diesel
198 engines by obtaining emission and fuel consumption values.

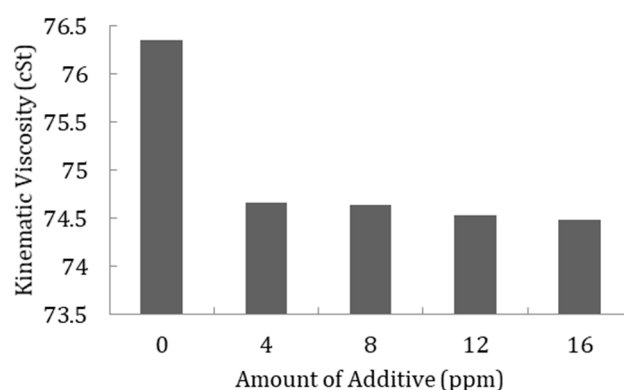
199 2.3. Error analysis and uncertainties

200 In the present study, error analysis of the measured and derived values was conducted and
201 uncertainties were also determined by using Kline and Mc. Clintock's method [37]. As each value
202 was measured three times, student's t-distribution was applied to the experimental data. Through
203 the evaluation of measured data, uncertainty intervals of fuel consumption, stable oil temperature,
204 smoke density and particle matter values were determined at the levels of (0.1-0.5)%, (0.08-0.6%),
205 (1.11-3.5)% and (0.1-6.5)%, respectively. From these results, it can be concluded that the probable
206 uncertainties in the measuring of the principle values and in the derived values would not
207 significantly affect s the uncertainties of the numerical results.

208 3. Results and Discussion

209 3.1. Some Properties of the Obtained Test Fuel

210 The change in the kinematic viscosity value of the organic-based Mn additive dosed waste
211 mineral oil with respect to the amount of additive substance in the laboratory is as follows (figure 3).
212 A high pumping pressure was also needed with high viscosity value. The standard kinetic viscosity
213 of a standard diesel fuel and biodiesel at 40°C was in the range of 1.9 to 4.5 cSt and 3.5 to 5 cSt
214 respectively. [38]. According to the results obtained, although the additive was seen to have a
215 kinematic viscosity lowering effect, it was far from the standard values at present. Only mechanical
216 filtration has been done since the intended use of the waste engine oil was the target of the work
217 being done. The kinematic viscosity of the waste engine oil could be reduced after different processes,
218 but this increases the operating costs considerably. However, the effect of Mn addition on the
219 kinematic viscosity after a certain dose is very small. Waste engine oil is only filtered and cleaned
220 additive was added.



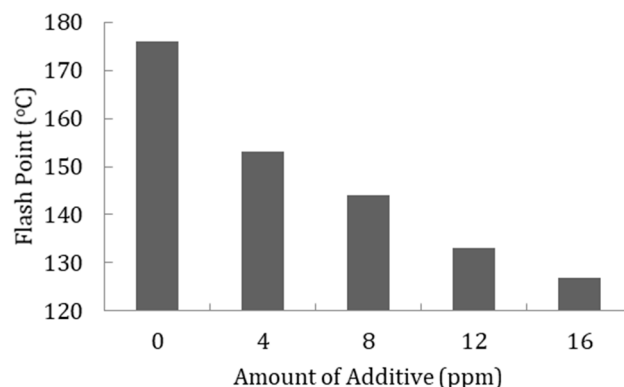
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222 **Figure 3.** Effect of organic-based Mn additive on kinematic viscosity

223 If a process for reducing viscosity was performed independently of the additive for waste engine
224 oil, the kinematic viscosity of the fuel obtained with the additive material would be approximated to
225 the standards.

226 The minimum temperature at which there is a sufficient concentration of evaporated fuel in the
227 air for the flame to propagate after an ignition source has been introduced is defined as the flash

228 point. Essentially, the flash point is the lowest temperature at which there is sufficient fuel vapor to
 229 give a momentary flash. It is one of the major flammability indices used to establish the fire and
 230 explosion hazards of liquids. The minimum limit values for the flash point are standard. When the
 231 effect of the Mn additive on the ignition point of waste engine oil was examined, it was seen that the
 232 additive was a reducing effect of the flash point (figure 4).
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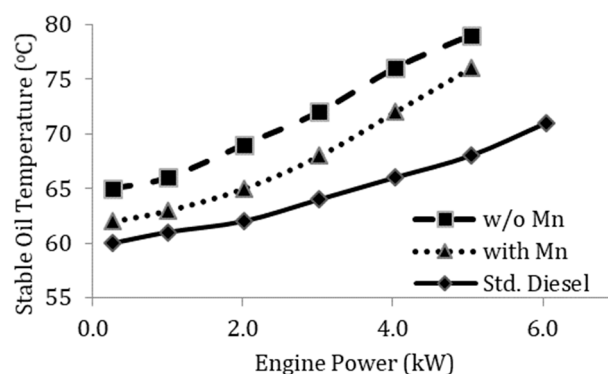
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Figure 4. Effect of organic-based Mn additive on flash point

236 The results from these laboratory tests were compared according to the EN 590 standard and
 237 were found to be close to the diesel fuel standards with the additive [32]. As a result of all these
 238 experiments, it was decided to use the 16 ppm organic-based Mn additive dosed waste oil in the
 239 experiments. After this step, engine performance and emissions were compared comparatively using
 240 the standard engine, unleaded waste lubricant, and additive waste mineral oil in the engine test set.

241 3.2. Effect of Mn Additive on Stable Working Temperature

242 In internal combustion engines, depending on the engine load, they work at an average
 243 constant temperature with the effect of the cooling system. In air-cooled engines, there are air fins for
 244 cooling and a fan that provides air flow to these air fins. The generator used in the experiments has
 245 cooling fan blades on the flywheel. The flow rate of the cooling air is constant as the engine is operated
 246 at constant speed. In the experiments, the oil temperature was taken as the reference for reaching the
 247 stable working (or oil) temperature of the engine. After a short time (approximately 25 minutes), the
 248 oil temperature became constant (Figure 5). The air flow rate in the engine cooling system remained
 249 constant as the engine was run at a constant speed during all the tests. The stable temperature values
 250 obtained in this study varied depending on the fuel characteristic only at a certain load and constant
 251 engine speed.



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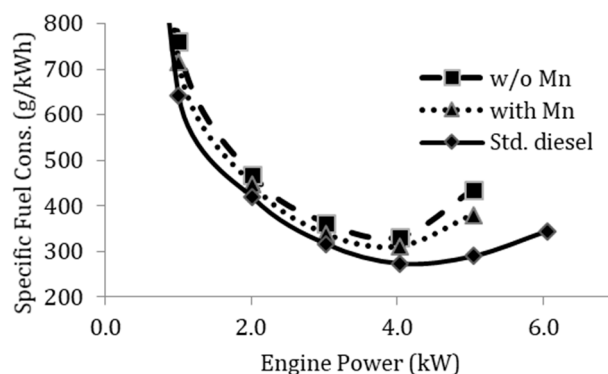
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Figure 5. Effect of organic-based Mn additive on stable working temperature

254 With Mn addition, the stable working temperature decreased by about 5%. The Mn additive has
 255 brought the stable working temperature of the waste mineral oil closer to the fuel of the engine. The
 256 reduction of the stable working temperature could be shown as the improvement of atomization by
 257 the effect of the reduction in viscosity together with the contribution of Mn additive and accordingly
 258 the improvement of the burn. Decreased fuel consumption with reduced stable working temperature
 259 was expected.

260 3.3. Effect of Mn Additive on Specific Fuel Consumption

261 Along with the use of waste mineral oil instead of diesel fuel, there was some decrease in engine
 262 speed. The fuel pump has been calibrated to regulate the engine speed again. For this reason, a slight
 263 increase in fuel consumption compared to diesel fuel had come to the fore. However, with the Mn
 264 additive, it seemed that fuel consumption had decreased somewhat. Along with the Mn additive,
 265 there were marked differences in the properties of the fuel such as viscosity and flash point. The effect
 266 of these differences was observed in the fuel consumption and specific fuel consumption as well as
 267 in the stabilized temperature (Figure 6).
 268



269 **Figure 6.** Effect of organic-based Mn additive on specific fuel consumption

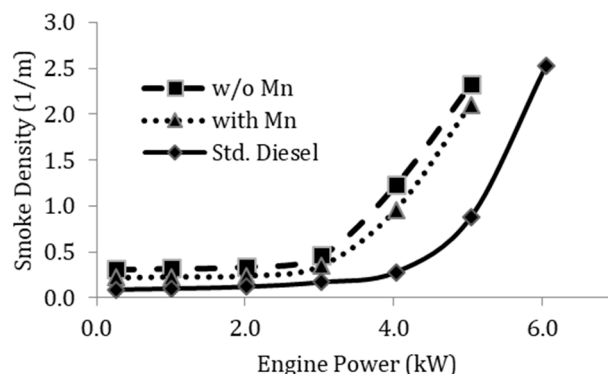
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Along with the Mn additive, less fuel was consumed for the same engine load. Given the decrease in stable working temperature, it was shown to decrease in lost heat. Specific fuel consumption, which is another expression of thermal efficiency, has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

276 3.4. Effect of Mn Additive on Exhaust Emission

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

282 Smoke density is defined as the percentage of non-transparent particles in the exhaust gas that
 283 reduce the intensity of the light they pass through when crossing the section [40]. However, another
 284 indicator of smoke density is the light absorption coefficient. Smoke density and the light absorption
 285 coefficient are two emission indices with the same tendency. Light absorption coefficient is limited
 286 to 2.5-3 m⁻¹ in diesel engines. These limits also apply to generator engines [41] (Figure 7).
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Figure 7. Effect of organic-based Mn additive on smoke density

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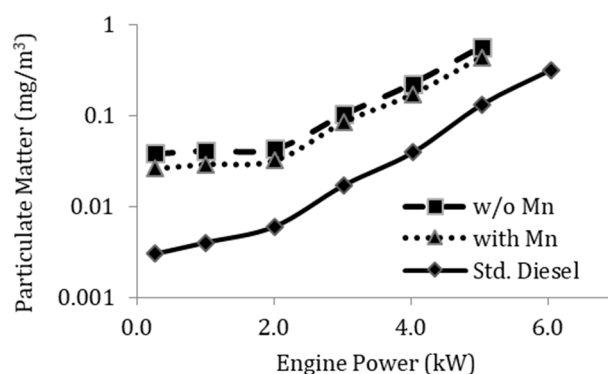
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The smoke density in experiments with diesel fuel at high engine loads was at normal levels. However, when waste mineral oil was used, it was not possible to measure smoke density because of the tendency of the engine to stop with high engine loads and excessive smoke. Along with the Mn additive, there was a decrease in the smoke density for the same engine load. When the amounts of the particulate matter were compared, it was seen that the Mn addition was also the effect of reducing the amount of the particulate matter (Figure 8).



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Figure 8. Effect of organic-based Mn additive on particulate matter

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4. Conclusion

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The effects of organic-based metal additives on engine performance and emissions have been observed in previous studies for biodiesel fuels derived from the engine oils and different vegetable and animal oils in previous studies [29-35,42-44]. However, studies on waste mineral oils have focused on the recycling of waste mineral oils after different chemical and mechanical processes [15, 45-48]. 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 degree of improvement with organic-based Mn additive material was investigated experimentally using a diesel engine with a power of 6.4 kW. Characteristic measurements were made for a constant speed (3000 rpm) and a variable load (750 W-4.5 kW) with an alternator rated at 5 kW. The kinematic viscosity of the waste oil used was too high compared to standard diesel fuel. High kinematic viscosity caused poor atomization of the fuel, poor combustion, clogging of the injectors, and carbon buildup in the segments. High viscosity required a high pumping pressure and the injector spraying was reduced. Experiments confirmed this information. It can be said that the effect of Mn addition on the flash point of the waste oil was a positive effect. However, the flash point was generally related to the storage and safety of the fuel. There was no effective change in engine performance. In addition,

316 changes in the flash point did not significantly affect the combustion characteristics. For the stable
317 working temperature, the oil temperature was used as a reference. The engine used in the
318 experiments was air-cooled and the cooling load was constant for constant engine speed. For this
319 reason, the stable working temperature was a clear indication of engine heat loss. The steady working
320 temperature of standard diesel fuel was even lower, although the stable working temperature with
321 Mn addition decreased somewhat. Since high viscosity negatively affected fuel atomization, the same
322 tendency could be seen in specific fuel consumption. Although the specific fuel consumption of diesel
323 fuel was the lowest in experiments made with fuels with the same thermal values, it can not be ruled
324 out that the Mn additive has a detrimental effect on the specific fuel consumption of the waste oil.

325 As a result, when evaluated in terms of engine performance and emissions, it appears that waste
326 mineral oils are not directly usable in diesel engines, especially in systems operating under constant
327 and stable conditions, such as generators. However, with the organic-based Mn addition, the fuel
328 characteristics of the waste mineral oil were closer to the engine. In conjunction with this study, it has
329 been possible, in part, that the organic-based Mn additive can be used in diesel engines.
330 Economically, both waste oil and additives do not cost much to be tested. An economic value can be
331 obtained with the development of this study. As a result of the work being done, it has been
332 understood that critical fuel properties such as viscosity should be improved by passing the waste
333 engine oils through different processes instead of using them directly. In subsequent work, additives
334 of different types of metal oxides can be tested by adjusting the viscosity of the waste engine oil
335 according to the standards. However, a more detailed examination can be made by performing
336 internal cylinder pressure measurement and combustion and heat emission analysis.

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345 experimental results.

346 **Conflicts of Interest:** The authors declare no conflicts of interest

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