

## AN IMPROVEMENT OF DIESEL FUEL WITH BIODIESEL ADDITION

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### Abstract

Whereas reducing the ratio of sulphur in diesel fuel yields the desired outcomes, it causes a decrease in its lubricity. Besides, with the causes of; the decrease happening in the viscosity depending on the increase in the temperature and the new injection systems working under high pressure conditions, the need is felt to include additives, high lubricity with environment-friendly, into the diesel fuel. In this study, the lubricity of the mixtures of the diesel fuel and the biodiesel volumetrically added at the rates of 4%, 20%, and 50% were determined by HFFR and pin-on-disc wear test method. It has been determined that the biodiesel additive dramatically improved the lubricity of the diesel fuel. With the advantage of biodiesel being a fuel on its own, it is being recommended as an additive to improve the lubricity of diesel fuel.

**Key Words:** Biodiesel, Lubricity, HFRR, Pin-on-disc.

### 1. Introduction

The serious restrictions on polluting emissions for the fossil fuels getting used up and the environmental reasons directed researchers to alternative energy resources. Especially, the need to reduce the exhaust emissions of the diesel engines has helped maintain the development of the diesel engine technology. These developments are in progress in the areas of diesel fuel injection technology, combustion after injection technology, and fuel production in higher standards [1].

The 5000ppm ratio of sulphur in the diesel fuel before 1993 has been, for environmental reasons, rendered mandatory to be reduced to below 500ppm by the United States Environmental Protection Agency (EPA). With the high technology used by the petroleum refineries, even this value has been reduced to the level of 15ppm and recently it has been aimed to reduce it to 10ppm [2]. With the restrictions brought to the burning-end products, but reducing the sulphur ratio in the fuel provided the desired outcome in terms of exhaust emissions, there were lubrication problems on the moving parts of the injection pump and in the injections lubricated by the fuel and this caused deterioration in the performance of the engine [3]. In 2010, in EU, for the regulations made to reduce the sulphur ratio to below 10ppm and the new injection systems working under high pressure conditions, intensive researches on the issue of including environment friendly additives into diesel fuel have been initiated.

The problem in the lubricity of the diesel fuel does not only stem from the reduction in the sulphur ratio, but also, depending on the heat, because of the reduction occurring in the viscosity, the fuel pump is not lubricated in the desired fashion [4]. Fuel spray in the diesel engines happens in the few-millisecond working period of the fuel pump. However, in this short interval, the pump is to increase the fuel pressure to 900-2000 bar depending on the fuel pressure, regulate the amount of fuel, and prepare itself for the coming courses. The manufacture of the fuel pump, which is considered to be the heart of the diesel engine, requires high technology, and it is highly important that it be lubricated thoroughly to provide the best working conditions during the operation of the engine.

It has been proved that by using a clear fuel with low sulphur ratio, lower ratios of nitrogen and aromatic

hydrocarbon emissions can be achieved through catalytic converters. But, when the fuel with low sulphur ratio is used, sufficient lubrication for the fuel injection system cannot be achieved. Because the fuels with low sulphur content, 15ppm, have less lubricity than the fuels with 500ppm sulphur content [5-7]. Researches show that sulphur-free, non-toxic, degradable, oxygenic, and renewable biodiesel provides perfect lubricity, and the addition of volumetric 1-2% biodiesel into diesel fuel helps the improvement of lubricity up to 60% [2].

There are many ways used to determine the lubrication performance. These are; vehicle test, fuel injection material bench test, and laboratory test. Since the first two methods require long operation time, and since the laboratory tests are more dependable, HFRR (High Frequency Reciprocating Rig) and SLBOCLE (Scuffing Load Ball On Cylinder Lubricity Evaluator) methods are widely being used [8,9-11]. Except these, MROCLE (Munson Roller On Cylinder Lubricity Evaluator), SRV (Optimal Reciprocating Rig), and BOTD (Ball-on-Three Disc) are also being used [2,8-10]. Engine manufacturers prefer the HFRR method more because it serves as a better indicator in terms of lubricity [5,12]. The lubricity of the fuels is to be in between the limits determined by the Engine Manufacturers Association (EMA). For example, in SLBOCLE test method (according to the ASTM D 6078 standard), it is expressed that 3100g is an appropriate value, and 2800g is an acceptable value for lubricity [13]. In HFRR test method (according to the ASTM D 6079 standard), the wear scar diameter (WSD) is accepted to show enough level of lubricity when it is below 380 $\mu$ m at 25°C, or below 450 $\mu$ m at 60°C. The assessment of BOTD method, on the other hand, is carried out through comparison with the upper limit of 450 $\mu$ m like in the HFRR method.

In the measurements made according to HFRR method by Schumacher et al., it has been seen that 2% biodiesel additive into diesel fuel reduced the wear scar diameter from 513 $\mu$ m to 200 $\mu$ m, providing an improvement of 60% [2]. Since polar ester groups in biodiesel can stick on the metal surfaces, quality surface lubrication is provided [14]. As a result, when the amount of sulphur in diesel fuel is reduced to 10ppm level, biodiesel additive as a solution to the lubrication problems occurring in the fuel injection systems operating with high pressure seems to be an important alternative.

In this study, lubricities of biodiesel fuels were investigated, and wear scars were examined by using HFRR test method and pin-on-disc type standard abrasion machine. Biodiesel additive was shown to improve the lubricity of the diesel fuel.

## 2. Material and Method

In this study, the lubricity of the fuel mixtures, which were made by adding biodiesel in the volumetric rates of 4%, 20%, and 50% into diesel fuel, were determined by using HFRR test method in Tübitak Marmara Research Center (Marmara Araştırma Merkezi, MAM), and it was compared with the lubricity of diesel fuel. Besides, by using the diesel fuel of the biodiesel used as a lubricant in this study, in pin-on-disc type standard abrasion machine with its 50% concentrations, the volume of wear on the samples, which is made of cast iron, has been determined. In HFRR test method, worn test (metal) balls and samples worn in pin-on-disc type abrasion machine were scanned and examined through an optical microscope.

HFRR method is a system where, under finely controlled conditions, the lubricity of a fluid is assessed by the measurement of the scars occurring on the surface of a test ball periodically reciprocating on a plate sunk into a fluid. Some experimental parameters used in HFRR are shown on Table 1.

Table1. Some experimental parameters used HFRR test process [15].

| Specifications              | Value |
|-----------------------------|-------|
| Temperature (°C)            | 60    |
| Specimen volume (mL)        | 2     |
| Load (g)                    | 200   |
| Humidity (%)                | >30   |
| Test duration (min)         | 75    |
| Frequency (Hz)              | 50    |
| Reciprocating distance (mm) | 1     |

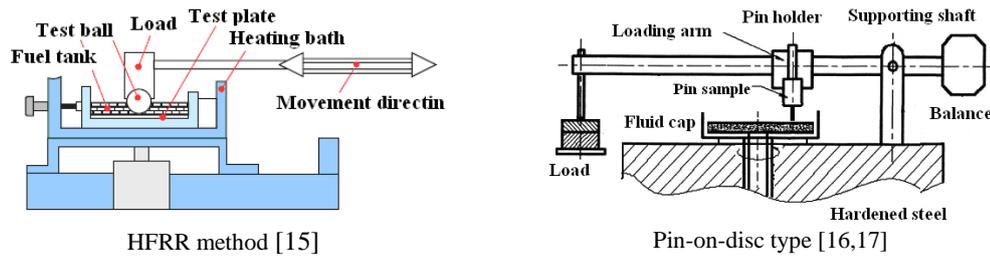


Fig. 1. Schematic diagram of wear testing rigs.

The schematic diagrams of HFRR and pin-on-disc type standard wear test rig used for experiments are shown in Fig. 1. In standard Pin-on-disc type abrasion machine, wear is provided by applying load on the surface of the sample which is being touched on a disc rotated by an electrical engine. Abrasion experiments have been made in a standard Pin-on-disc type device by slipping the samples, made of cast iron with the radiuses of 10mm, for 3000m in a mixture of volumetric 50% watermelon seed, melon seed, soy oil, and flax seed oil methyl esters with diesel fuel, and under a load of 3150g. Before the experiment began, the surfaces of the samples had been rubbed with SiC sandpaper of 1200µm and weighted on a 0,1mg precision. After this process, the sample was placed in the holders, and so, prepared for the test. After zeroing the balance weight on the carrying arm and the load on the dowel, the desired force was applied by hanging weight on the carrying arm which is on the other end of the arm. The worn test balls and the samples were examined by the help of a optical microscope and the wears were compared. The results of the spectral analysis of the worn samples are shown in Table 2.

Table 2. Chemical composition of the cast iron used (wt.%)

|    |       |
|----|-------|
| C  | 2.90  |
| Si | 1.76  |
| Mn | 0.63  |
| P  | 0.063 |
| S  | 0.041 |
| Cr | 0.038 |
| Ni | 0.126 |
| Cu | 0.122 |
| Fe | 94.2  |

In tables and charts, “D2” stands for no.2 fuel, “F” stands for flax seed oil methyl ester, “WM” stands for watermelon seed methyl ester, and “M” stands for melon seed methyl ester. Besides, XX number shows the percentage of the amount of biodiesel in the mixture. For example, 50WM denotes a mixture of 50% biodiesel, and 50% diesel fuel. The specifications of biodiesel and diesel fuel no. 2 are shown in Table 3.

Table 3. Fuel specification used in the experiment

| Specifications                                   | Diesel fuel <sup>a</sup> | MSOME <sup>b</sup> | WMSOME <sup>b</sup> | FSOME <sup>b</sup> |
|--|--------------------------|--------------------|---------------------|--------------------|
| Density, kg/m <sup>3</sup> , at 15°C             | 828.0                    | 887.1              | 894.2               | 900                |
| Kinematic viscosity, mm <sup>2</sup> /s, at 40°C | 2.6                      | 4.824              | 6.413               | 5.224              |
| Sulfur content, mg/kg                            | 56 (22ppm)               | 2.0                | 2.3                 | 19.9               |
| Copper strip corrosion, 3h at 50°C               | -                        | 1a                 | 1a                  | 1a                 |
| Acid number, mg KOH/g                            | -                        | 0.07               | 0.10                | 0.14               |
| Iodine number, g iodine/100 g                    | -                        | 117                | 121                 | 171                |
| CFPP, °C   | -5                       | -5                 | -4                  | -11                |

<sup>a</sup> These are standard values taken by Shell Company.

<sup>b</sup> Measured by Petroleum Research Center Laboratory at METU, Ankara, Turkey.

### 3. Results and Discussion

Many methods are being used to determine the lubricities of the fuels. Among these methods, being a better lubricity indicator, and giving more reliable results in a short time, HFRR method has been the preferred one by the engine manufacturers. In this study, the lubricities of the diesel fuel and its mixtures with the biodiesel have been examined by both the HFRR, and the pin-on-disc methods. The measurement results, made by HFRR test method in Marmara Research Center, of the lubricities of the fuel samples are seen on Fig. 2. It has been determined that, by adding biodiesel, the lubricity of the diesel fuel is improved significantly and the diameter of the wear scar is decreased. It has been seen that biodiesel improves the lubricity of the diesel fuel, and this improvement changes accordingly with the ratio of biodiesel in the mixture. It has been observed that a 45% improvement, with respect to the lubricity value of the diesel fuel, is provided in the lubricity of the 50% biodiesel-diesel fuel mixtures. The lubricities of the biodiesels produced from different

sources can differ from each other since the lubricities are interrelated with the chemical structures and the viscosities of the oils. However, it has been determined that biodiesel can be used as an effective lubricate additive in diesel fuels because it has better lubricity than standard diesel fuel. Biodiesel can be used by mixing its pure form or its diesel fuel in any ratios, and by making no changes whatsoever in the engine or just by making a little modification. According to Knothe and Steidley (2005), even in quite low ratios of biodiesel addition increase the lubricity of the diesel fuels [8]. Since it improves the lubricity, 2% biodiesel addition into the diesel fuel is recommended [18].

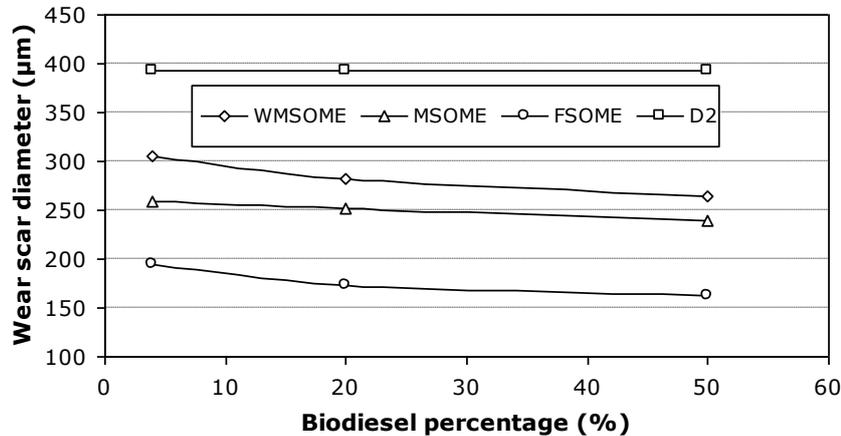


Fig. 2. Effect of biodiesel percentage on lubricity.

In Fig. 3, you can see the optical microscopic views of the test balls used in determining the lubricities of the fuels by HFRR method. It is seen that the scars are longer in perpendicular axis to the friction direction, shorter in horizontal axis, and there is a color change around the scars with the rise in the heat. While there occurred a wider scar on the worn test ball in D2 fuel where there was not so good lubrication (Fig. 3a), it has been observed that, there occurred a narrower scar on the test ball worn in 50F fuel (Fig. 3b). In the measurements done with the test fuels, the wear scar diameters have been found in between 163-393µm. Since the wear scar diameter below 450µm shows the sufficient amount of lubricity according to the ASTM D 6079 standard, in HFRR method, the measured values are in the acceptable limits [11]. In Fig. 3c and d, you can see the difference between the wear scars of the two different biodiesels added, in equal amounts, into a diesel fuel.

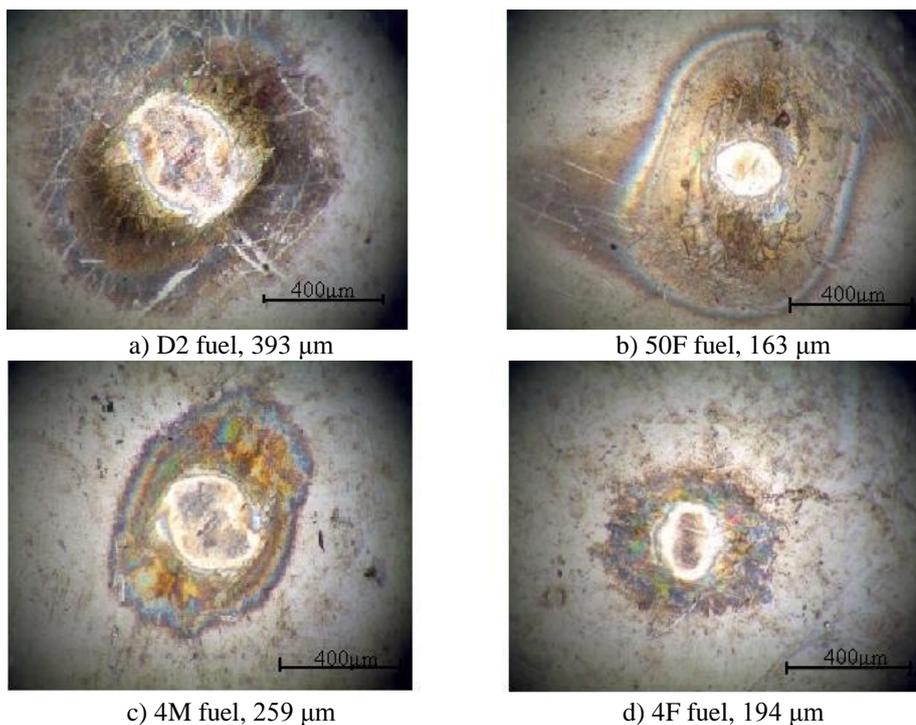


Fig. 3. The pictures of some test balls worn in HFRR test.

In the experiments conducted in Pin-on-disc type standard abrasion machine, the best-lubricity-value diesel fuel of the biodiesel, its 50% concentration, and the best-lubricity-value flax seed oil methyl ester diesel fuel and its 5% concentration were used. The volumes of scars are shown in Fig. 4, and the worn surfaces are shown in Fig. 5.

The highest volume of scars was seen to be occurred when the diesel fuel was used as a lubricant and then 50WM, 50M, 5F, 50F fuels were used respectively. It was observed that even the 5% mixture of the best-lubricity-value flax seed oil methyl ester had proved better lubricity than the other fuel concentrations. When %50F concentration used, there occurred a significant rate of decrease in the volume of scar, Fig. 4.

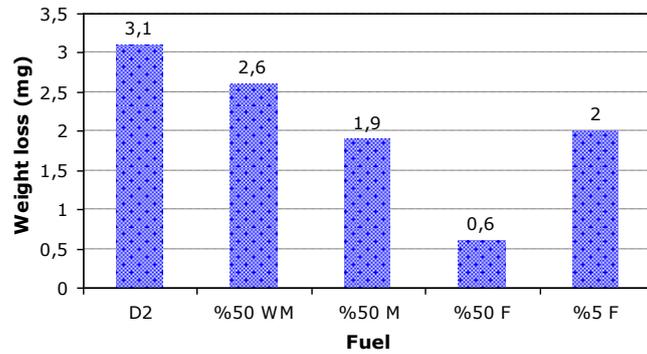


Fig. 4. The weight loss of the samples worn in the pin-on-disc type abrasion machine.

In Fig. 5, optical microscopic views of the worn samples in the pin-on-disc device are given. Seen in these figures, generally the wear occurred in the formation of a scar.

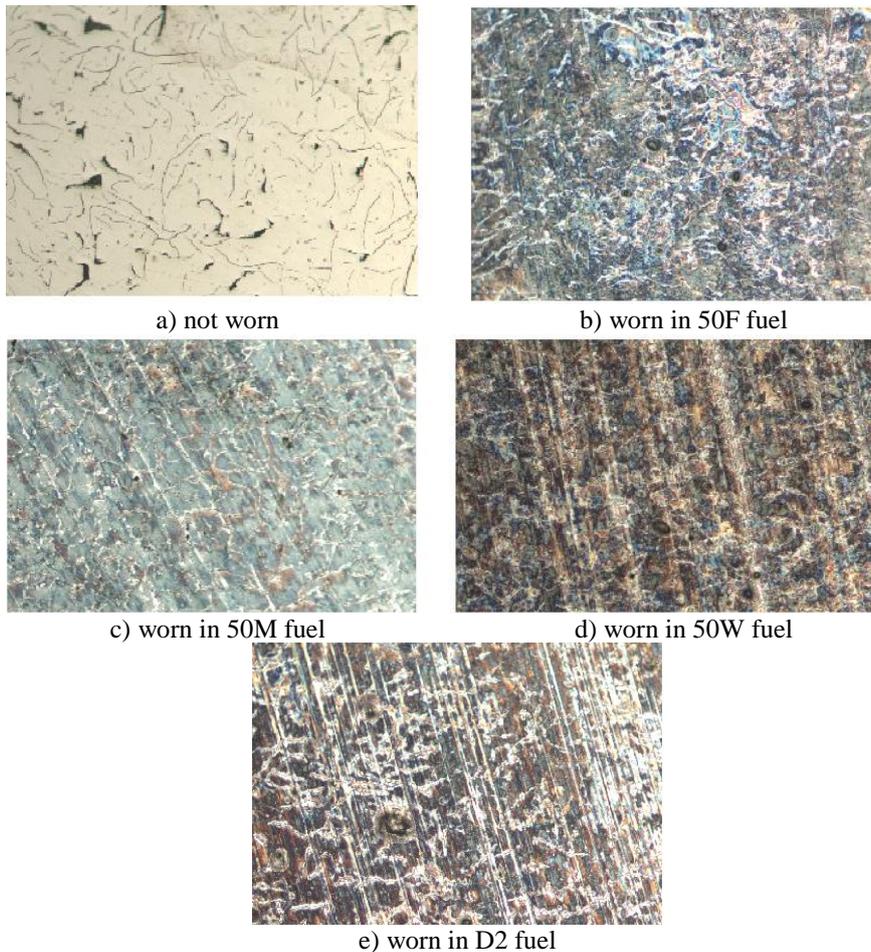


Fig. 5. Microscopic views of some samples worn in Pin-on-disc type wear testing machine.

While the least volume of wear occurred in 50F fuel (Fig. 5b), the highest volume of wear was observed on the sample worn in D2 fuel (Fig. 5e). The wear scars occurred on the worn samples happened to become more distinctive on the surfaces of the samples worn in 50M fuel with respect to the scars on the surfaces of the ones worn in 50F. The scars occurred on the samples worn in 50WM fuel happened to concentrate a little more and become more distinctive. On the surface of the sample worn in D2 fuel, however, it was seen that the wear increased, and the scars were deeper and denser.

The viscosity of the diesel fuels is demanded to be low enough to flow freely in low working temperatures, high enough to avoid leaking and lubricate the injector system, and proper to be easily atomized into the combustion chamber. While the feature of having a higher viscosity makes biodiesel a perfect lubricate additive, the bubble-size buildup during the spray prevents the atomization to occur properly [19-22].

#### 4. Conclusion

Since the injection system is lubricated by the fuel while many parts of the engine are lubricated by lubricant, the lubricity of the fuel must be in the limits determined by Engine Manufacturers Association (EMA). Biodiesel can be produced from renewable resources like vegetable, animal and waste oils, and can be used in pure form or in a mixture with the diesel fuel in diesel engines without making any adjustment or change. Adding even in low ratios of biodiesel into diesel fuel increases the lubricity significantly. In this study, the lubricities of the biodiesel fuels were investigated and the following results were obtained.

- The reduction of sulphur in fuels decreases the lubricity; this decrease can be compensated by using vegetable oils; being a fuel on its own, biodiesel can improve the lubrication performance.
- In the experiments where biodiesel is added into diesel fuel, the wear scar diameter falls below 230µm; that is, the lubricity increases at a significant level and biodiesel is a potential additive for improving the lubricities of low-sulphur rated diesel fuel.
- In the experiments done in the pin-on-disc type standard abrasion machine, the highest rate of wear occurred when the diesel fuel was used. On the surfaces where there was not good lubrication, it was observed that the heat increased and the deformation deepened.
- The results from the HFRR test method and pin-on-disc abrasion machine were coherent. It was determined that the lubricity of diesel fuel improves by adding biodiesel into diesel fuel.
- Beyond the mentioned advantages, while the waste oils are recycled by using biodiesel for the improvement of the lubricity of diesel fuel, contaminating exhaust emissions will be reduced –not completely but– partially. Besides, greenhouse gas emissions will be reduced, it will help reduce the dependence of the nation on foreign sources in terms of petroleum consumption, it will support the agriculture, and it will create market opportunities for the new products. These results have been achieved through quite a number of studies.

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