Article

The Impact of Fatty Acid Diisopropanolamides on Marine Gas Oil Lubricity

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Abstract: In this study, seven mixtures of diisopropanolamides that were synthesized from various vegetable oils (sunflower oil, soybean oil, cotton seed oil, olive oil, tobacco seed oil, coconut oil, used frying oil) were used as lubricating additives in a low-sulfur marine gas oil. All tribological measurements were carried out by using the high-frequency reciprocating ring (HFRR) test procedure, according to EN ISO 12156-1. The obtained wear results showed that all mixtures of diisopropanolamides used provide satisfactory a mean wear scar diameter (WS 1.4) of less than 520 µm, at concentration levels of 60–120 ppm. The concentrations below 60 ppm had no effect on the fuel lubricity. An increase in the concentration of the diisopropanolamide mixtures led to an insignificant increase of the lubrication effectiveness.

Keywords: Marine Gas Oil; lubricity; lubricating additives; diisopropanolamides; HFRR

1. Introduction

It is well known that the maritime transport has an impact on the global climate and on air quality. In order to reduce the carbon dioxide (CO₂) emissions and other ship emissions, such as nitrogen oxides (NOₓ), sulphur oxides (SOₓ), methane (CH₄), particulate matter (PM) and black carbon (BC), stricter regulations have been implemented [1]. The Californian Air Resource Board (CARB) has since 1 July 2009 enforced the use of Marine Diesel Oils (MDOs) or Marine Gas Oils (MGOs) in Californian waters [2]. In addition, when in berth in EU ports, as of 1 January 2010 vessels must use marine fuels with a sulfur content not exceeding 0.1% by mass [3].

The practical effect of the above pollution control regulations is to oblige many ships to switch from viscous high-sulfur heavy fuel oil to thin distillate fuels such as MGO. However, there is a technical difficulty. The fuel pumps in marine engines are designed to run under full-film conditions. The basic tribological concept is that the oil film will carry the load of the movement. In order to achieve the optimized working conditions, the viscosity of the fuel must be high in order to carry the radial forces produced by the high-speed operation. Additionally, another important factor is the working differential pressure. Higher differential pressure results in higher radial forces. The failure prevention will be achieved only if full-film working conditions have been taking place [4,5].

When a three-screw pump operates with light fuel such as MDO or MGO, the above condition has not been fulfilled, and as a result the operation of the pump is not the preferable one (boundary
This means that the metallic parts have been working in closer contact. When this condition occurs, the lubricity of the fuel has high importance in order to prevent seizure failure [4,5].

It is still the case that lubricity is poorly understood in the marine sector, with many misconceptions existing in the aftermath of the publication of the new specification. The same situation occurred in the early 1990s, when low-sulfur diesel fuels were introduced to the automotive market; lubricity was likewise poorly understood, and field issues rapidly followed, involving excessive and rapid fuel pump wear [6].

It was established through the past years that the ship engineers must use marine fuel with high viscosity in order to prevent failure from wear. This rule is not applicable since the introduction of low-sulfur marine fuels. It was proved that even low-sulfur marine fuels with high viscosity have the ability to produce wear problems [7].

Polar compounds which were formed through the production process provide a protection layer between the working metal surfaces. The heterocyclic oxygen, nitrogen, and aromatics compounds are basically contributed to the protection rather than the sulfur compounds [8–10]. It is well-known the hydrocarbon fuels are complex mixtures. It is evident that some compounds of marine diesel fuels are more active in this protection mechanism than others. On the other hand, the legislation in force set the obligation for lower sulfur levels. The hydrotreating process is necessary in order to lower the sulfur levels in the fuels. Simultaneously, this process destroys a number of the above-mentioned natural lubricants. The overall modern refinery processes also affects the concentration of the lubricity agents in the final commercial diesel fuel [11]. As a result, and in order to prevent this problem, lubricity additives have been developed and produced to compensate the deterioration in the lubricity of the marine diesel production. When a suitable additive is used, the appropriate dosage range must be used. If this rule is not followed, the fuel additives can lead to an injector failure or to an engine failure through the injector deposits, water separation, and filter plugging. These problems will be identified during the operation, and they are largely known as field or operational problems [12–15].

This study includes the evaluation of the lubricating properties of low-sulfur marine gas oil, additized with seven mixtures of fatty acid diisopropanolamides. The scope of this effort is to identify the minimum concentration of the above compounds. The basic criterion is to provide lubricity improvement down to the 520 µm wear scar diameter level. The value of 520 µm was the minimum threshold for an acceptable field performance as proposed by the International Organization for Standardization (ISO) and generally adopted by the industry [16].

It is well-known that fatty acids and their derivatives are superior friction-reducing agents [17–31]. The main purpose of these oxygen compounds is to reduce adhesion between contacting asperities and to limit friction, wear, and seizure. This can be achieved because they adsorbed or reacted with the rubbing working surfaces. Wei and Spikes considered that a significant wear protection will be provided if additives with oxygen compounds with phenolic-type or carboxylic acid groups were to be used in low concentration (parts per million, ppm) [32].

Although the impact of amides and acid esters on the lubricity of automotive diesel has been closely examined, their impact on the tribological behaviour of low-sulfur middle distillate gas oils which are mainly used in marine compression ignition engines has not been examined in appropriate detail.

2. Experimental Procedure

2.1. Materials

Bis(2-hydroxypropyl) amine, sodium methoxide, and analytical reagents such as the standards for gas chromatography (GC) analysis were of high grade and were supplied from Sigma-Aldrich Chemie GmbH. (Taufkirchen, Germany) Commercial grade olive oil, soybean oil, and sunflower oil were purchased from a local commercial grocery store (Athens, Greece). Cottonseed and coconut oil were obtained from Elin Biofuels S.A. (Volos, Greece). The waste vegetable oil used in this work was
a mixture of olive oil and sunflower oil which were collected from local fast food restaurants from a business activity of Elin Biofuels S.A. The tobacco seed oil that was not commercially available was extracted from tobacco seeds in laboratory scale, following a specific procedure, which is as follows. The seeds were ground to a fine powder and then dried for 2 h at 100 °C. For the continuous extraction of a solid by a hot solvent, the Soxhlet extraction apparatus was employed. Hexane was used as a solvent in the extraction process where the temperature was kept at 65–70 °C, and the overall process lasted 4 h. At the end of the process, the oil was separated from the organic solvent using a rotary vacuum evaporator, dried at 60 °C, and weighed. The seven vegetable oils were used as received without further purification. Table 1 gives their fatty acid profile.

In order to assess the impact of the selected mixtures of diisopropanolamides on the lubrication properties of low-sulphur marine fuels, as base fuel for all of the tribological experiments, a commercially-available MGO was used (obtained by a Motor Oil Hellas Corinth Refineries S.A (Corinth, Greece) in an appropriate quantity). The fuel properties are presented in Table 2, along with the standard methods that were used for their determination.

2.2. Preparation of Diisopropanolamides

The preparation reaction of diisopropanolamides was carried out in a round-bottom glass reaction flask submerged in an oil bath. The reaction flask was equipped with a mechanical stirrer, a thermometer, and a condenser. Bis(2-hydroxypropyl) amine was reacted with the oils at a molar ratio of 6:1 (bis(2-hydroxypropyl)amine:oils) in the presence of sodium methoxide (2% by weight of bis(2-hydroxypropyl)amine and oil). The reactions were carried out at a temperature of 140 °C, while the formation of diisopropanolamides was monitored using thin layer chromatography. The reaction mixture was naturally cooled and dissolved in diethyl ether in a separating funnel.

2.3. Lubricity Measurements

All tribological measurements were carried out using the High-Frequency Reciprocating Ring (HFRR) apparatus (Figure 1), according to the EN ISO 12156-1 method. The standardized test temperature was 60 °C and the accurate volume of the fuel sample used was 2 mL. In order to obtain reproducible and reliable results, the relative humidity was kept between 51% and 53%, while the mean ambient temperature was 21 ± 0.2 °C. The lubricating efficiency of the fuels was estimated by measuring the average Wear Scar Diameter (WSD) of the spherical specimen by using a photomicroscope. The wear scars quoted were corrected to give the Wear Scar (WS) 1.4 values for evaluation. The HFRR WS 1.4 parameter is the mean WSD normalized to a standard vapour pressure of 1.4 kPa. The repeatability was calculated using the following Equation (1) [16]:

\[ R = 139 - (0.1648 \times WS \text{ 1.4}) \] (1)

The seven diisopropanolamides mixtures were dissolved in the base fuel at the concentration levels of 20, 40, 60, 80, 100, 120, 140 and 160 ppm.
Table 1. Fatty acid profile of vegetable oils, % m/m.

| Fatty Acid     | Chemical Structure | Vegetable Oil Type | Sunflower Oil | Soybean Oil | Olive Oil | Cottonseed Oil | Coconut Oil | Used Frying Oil | Tobacco Seed Oil |
|----------------|--------------------|--------------------|---------------|-------------|-----------|----------------|-------------|-----------------|------------------|
| Lauric (C12)   | CH$_3$(CH$_2$)$_9$COOH | 0.00               | 0.10 ± 0.01   | 0.00        | <0.01    | 49.20 ± 0.02  | 1.98 ± 0.01 | 1.98 ± 0.01     | <0.01            |
| Myristic (C14) | CH$_3$(CH$_2$)$_11$COOH | 0.00               | 0.10 ± 0.01   | 0.00        | 0.75 ± 0.01 | 18.50 ± 0.02  | 0.32 ± 0.01 | 0.09 ± 0.01     | <0.01            |
| Palmitic (C16) | CH$_3$(CH$_2$)$_14$COOH | 6.20 ± 0.01        | 11.30 ± 0.01  | 11.60 ± 0.01| 22.23 ± 0.01| 9.10 ± 0.01   | 15.65 ± 0.02| 10.96 ± 0.01    | <0.01            |
| Palmitoleic (C16:1) | CH$_3$(CH$_2$)$_13$CH=CH(CH$_2$)$_7$COOH | 0.10 ± 0.01        | 0.00          | 0.90 ± 0.01 | 0.44 ± 0.01 | 0.10 ± 0.01   | 0.31 ± 0.01 | 0.20 ± 0.01     | <0.01            |
| Stearic (C18)  | CH$_3$(CH$_2$)$_16$COOH | 3.70 ± 0.01        | 4.10 ± 0.01   | 3.10 ± 0.01 | 2.17 ± 0.01 | 2.70 ± 0.01   | 3.10 ± 0.01 | 3.34 ± 0.01     | <0.01            |
| Oleic (C18:1)  | CH$_3$(CH$_2$)$_17$CH=CH(CH$_2$)$_7$COOH | 25.20 ± 0.01       | 22.70 ± 0.02  | 74.98 ± 0.03| 17.66 ± 0.02| 6.50 ± 0.01   | 48.71 ± 0.02| 15.54 ± 0.01    | <0.01            |
| Linoleic (C18:2) | CH$_3$(CH$_2$)$_17$CH=CH(CH$_2$)$_7$COOH | 63.10 ± 0.01       | 52.60 ± 0.01  | 7.80 ± 0.01 | 55.77 ± 0.01| 1.70 ± 0.01   | 22.39 ± 0.01| 69.49 ± 0.02    | <0.01            |
| Linolenic (C18:3) | CH$_3$(CH$_2$)$_17$CH=CH(CH$_2$)$_7$COOH | 0.30 ± 0.01        | 7.40 ± 0.02   | 0.60 ± 0.01 | 0.13 ± 0.01 | 0.00          | 1.04 ± 0.01 | 0.69 ± 0.01     | <0.01            |
| Ecosanoic (C20) | CH$_3$(CH$_2$)$_19$CH=CH(CH$_2$)$_9$COOH | 0.20 ± 0.01        | 0.50 ± 0.01   | 0.01        | 0.20 ± 0.01 | 0.10 ± 0.01   | 0.11 ± 0.01 | 0.25 ± 0.01     | <0.01            |
| Behenic (C22)  | CH$_3$(CH$_2$)$_21$COOH | 0.70 ± 0.01        | 0.50 ± 0.01   | 0.10 ± 0.01 | <0.01     | 0.10 ± 0.01   | 0.24 ± 0.01 | 0.12 ± 0.01     | <0.01            |
| Erucic (C22:1) | CH$_3$(CH$_2$)$_17$CH=CH(CH$_2$)$_11$COOH | 0.10 ± 0.01        | 0.20 ± 0.01   | 0.00        | 0.02      | 0.00          | 0.02 ± 0.01 | <0.01           | <0.01            |
| Lignoceric (C24) | CH$_3$(CH$_2$)$_22$COOH | 0.20 ± 0.01        | 0.20 ± 0.01   | 0.50 ± 0.01 | 0.01 (±<0.01) | 0.00         | 0.30 ± 0.01 | 0.04 (±<0.01)   | <0.01            |
was shown with the addition of the sunflower oil diisopropanolamides under observation in the Lubricants 2017, and the fuel attained a constant wear scar diameter value of approximately 515 $\mu$m. Yet, even in this case, the limit of 520 $\mu$m was not satisfied. When dealing with the increase of the concentration of sunflower oil diisopropanolamides from 100 to 120 ppm, it was observed that there was an increasing effect on the lubricity of the base fuel, thus decreasing the corrected wear scar diameter of the base fuel. A substantial increase of the lubrication performance diisopropanolamides that ranged between 20 and 80 ppm caused practically no alteration in the lubricity performance of the produced additives.

In order to determine the MGO lubrication ability along with its relative chemical characteristics, a fuel properties analysis was conducted. The results are presented in Table 2. The lubricity of the base fuel is poor, as demonstrated by the depicted results which are much higher than the upper limit of 520 $\mu$m. Additionally, this poor lubrication ability makes it a good base fuel in order to determine the lubricity performance of the produced additives.

Figure 2 gives a graphical representation of the effect of the addition of the sunflower oil diisopropanolamides mixture on the WS 1.4 of the base fuel. Small concentrations of sunflower oil diisopropanolamides mixture between 120 and 160 ppm, the decrease in the WSD values was small, and the fuel attained a constant wear scar diameter value of approximately 515 $\mu$m.

### Table 2. Properties of the base fuel.

| Property                  | Value              | Test Method                          |
|---------------------------|--------------------|--------------------------------------|
| Density (kg/m$^3$, 15 °C) | 853.5 ± 0.7        | EN ISO 12185 [33]                    |
| Kinematic Viscosity (cSt at 40 °C) | 3.27 ± 0.04        | EN ISO 3104 [34]                    |
| Flash point (°C)          | 64 ± 0.5           | EN ISO 2719 [35]                     |
| Nitrogen content (mg/kg)  | 31 ± 1             | -                                    |
| Sulfur content (mg/kg)    | 310 ± 8            | EN ISO 8754 [36]                     |
| Cloud point (°C)          | -3 ± 0.1           | ISO 3015 [37]                        |
| Pour point (°C)           | -9 ± 0.2           | ISO 3016 [38]                        |
| Ash content (% m/m)       | <0.01              | EN ISO 6245 [39]                     |
| Carbon residue (% m/m)    | 0.006 ± 0.0005     | EN ISO 10370 [40]                    |
| Water content (mg/kg)     | 29 ± 1             | ISO 3733 [41]                        |
| Cetane index              | 49.7 ± 0.1         | EN ISO 4264 [42]                     |

Lubricity

| Property                  | Value              | Test Method                          |
|---------------------------|--------------------|--------------------------------------|
| Initial measurement, μm   | 645 ± 1            | EN ISO 12156-1 [43]                  |
| Repeated measurement, μm  | 641 ± 1            |                                     |
| Distillation (°C)         |                    |                                      |
| Initial Boiling Point (IBP)| 177 ± 0.5         | EN ISO 3405 [44]                     |
| 10%                       | 231 ± 0.4          |                                      |
| 50%                       | 295 ± 0.4          |                                      |
| 90%                       | 352 ± 0.5          |                                      |
| Final Boiling Point (FBP) | 378 ± 0.5          |                                      |

Figure 1. Schematic diagram of lubricity test by high frequency reciprocating test rig.

3. Results and Discussion

In order to determine the MGO lubrication ability along with its relative chemical characteristics, a fuel properties analysis was conducted. The results are presented in Table 2. The lubricity of the base fuel is poor, as demonstrated by the depicted results which are much higher than the upper limit of 520 $\mu$m. Additionally, this poor lubrication ability makes it a good base fuel in order to determine the lubricity performance of the produced additives.

Figure 2 gives a graphical representation of the effect of the addition of the sunflower oil diisopropanolamides mixture on the WS 1.4 of the base fuel. Small concentrations of sunflower oil diisopropanolamides that ranged between 20 and 80 ppm caused practically no alteration in the corrected wear scar diameter of the base fuel. A substantial increase of the lubrication performance was shown with the addition of the sunflower oil diisopropanolamides under observation in the concentration of 100 ppm. Yet, even in this case, the limit of 520 $\mu$m was not satisfied. When dealing with the increase of the concentration of sunflower oil diisopropanolamides from 100 to 120 ppm, it was observed that there was an increasing effect on the lubricity of the base fuel, thus decreasing the wear scar diameter by 2 $\mu$m under the acceptable limit. For concentrations of sunflower oil diisopropanolamides mixture between 120 and 160 ppm, the decrease in the WSD values was small, and the fuel attained a constant wear scar diameter value of approximately 515 $\mu$m.
The impact of soybean oil diisopropanolamides on the lubricity of the base fuel is outlined in Figure 3. When analyzing the results, it is observed that even though it increased the lubricity of the base fuel, the addition of soybean oil diisopropanolamides mixture in concentrations between 20 and 100 ppm did not reach the acceptable limit value of 520 µm. The desired improvement was realized, as there was an increase in the concentration of soybean oil diisopropanolamides from 100 to 120 ppm, where the maximum permissible HFRR mean wear scar diameter for commercial marine fuels was satisfied.

Figure 2. Impact of sunflower oil diisopropanolamides addition on the lubrication properties of the base fuel. WS: wear scar.

Figure 3. Impact of soybean oil diisopropanolamides addition on the lubrication properties of the base fuel.
Figure 4 shows the influence of the olive oil diisopropanolamides on the lubrication properties of the base fuel. On the basis of the HFRR test results, the addition of olive oil diisopropanolamides mixture at the concentration levels lower than 80 ppm does not seem capable of increasing the lubricity of the fuel to an acceptable level. On the contrary, a significant reduction of the WS 1.4 to under the limit of 520 µm was observed when 80 ppm of olive oil diisopropanolamides mixture was added, whereas extra addition of diisopropanolamides seemed to offer an even better improvement of the lubrication properties of the base fuel. Thus, for concentrations between 100 and 160 ppm, the wear scar diameter illustrates an even higher decline, reaching 477 µm. Comparing tribological results that were obtained upon the addition of olive oil diisopropanolamides to the base fuel to those that resulted from the addition of sunflower oil diisopropanolamides, it is apparent that the olive oil diisopropanolamides mixture had a much better influence on the fuel lubricity. This may be due to the high content of mono-unsaturated diisopropanolamides like those of oleic acid and to the higher concentration of palmitic acid diisopropanolamide.

Figure 5 depicts the impact of the addition of cottonseed oil diisopropanolamides on the base fuel. Similarly, as in the case of the sunflower oil diisopropanolamides mixture, the required treatment rate to obtain a satisfactory wear scar diameter (WS 1.4) of 520 µm was 120 ppm. However, a higher dosage of the cotton seed oil diisopropanolamides led to a slight increase of the fuel lubricity. The careful assessment of the experimental results leads to the realization that cottonseed oil diisopropanolamides mixture presents a slightly improved lubrication performance compared to sunflower oil diisopropanolamides. Even though both types of diisopropanolamides provide an acceptable level of performance at 120 ppm, at this concentration level the corrected wear scar diameter of sunflower oil diisopropanolamides was 518 µm, while the WSD value of the cottonseed oil diisopropanolamides was 490 µm. Thus, the second mixture of diisopropanolamides had a slightly better lubrication performance. A possible explanation for this may be that cottonseed oil diisopropanolamides mixture contains a higher content in palmitic acid diisopropanolamide in comparison to sunflower oil diisopropanolamides mixture. Consequently, the slightly better lubrication effectiveness of cotton seed oil diisopropanolamides is possibly due to the presence of saturated fatty acids.
Figure 5. Impact of cottonseed oil diisopropanolamides addition on the lubrication properties of the base fuel.

Figure 6 presents the dependence of the base fuel lubricity on the concentration of coconut oil diisopropanolamides. Although their addition at concentrations lower than 60 ppm did not seem capable of achieving a WS 1.4 value well within the required limit, a notable improvement in the fuel lubricity was observed with the addition of 60 ppm of the diisopropanolamides mixture, where the wear scar diameter was decreased to 510 µm. It should also be noted that these esters presented the best effect on the lubrication properties of the base fuel from any other type of diisopropanolamides examined, thus enhancing the assumption that as the concentration of saturated and mono-unsaturated diisopropanolamides in the mixture is increased, so is the lubrication performance.

Figure 6. Impact of coconut oil diisopropanolamides addition on the lubrication properties of the base fuel.
Figure 7 illustrates the impact of the addition of used frying oil diisopropanolamides on the WS 1.4 of the base fuel. At first glance, this particular type of diisopropanolamides improves the lubrication properties of the base fuel. The analysis of the trend curve shows that the limit of 520 µm for the mean WS 1.4 can be attained at a diisopropanolamides mixture concentration of 100 ppm or more. When comparing the HFRR test results of used frying oil diisopropanolamides mixture to those of the diisopropanolamides that contain high levels of C18:2, one can draw the conclusion that the used frying oil diisopropanolamides mixture has better lubricating ability. The better behavior of this type of diisopropanolamides on fuel lubricity may be due to the higher total content of saturated and mono-saturated fatty acid diisopropanolamides, which, based on the results of Table 1, reaches about 70%.

Figure 8 demonstrates the effect of the addition of tobacco seed oil diisopropanolamides on the tribological properties of the base fuel. Similar behaviour to that of sunflower and cotton seed oil diisopropanolamides was presented by the diisopropanolamides of the tobacco oil. Generally, small concentrations between 20 and 100 ppm did not have a positive influence on the lubrication properties of the base fuel. The desired improvement was achieved at the concentration of 120 ppm. Any increase in tobacco seed oil diisopropanolamides mixture concentration led to a slight increase in the wear scar diameter values. It must be noted that tobacco seed oil diisopropanolamides mixture have a slightly worse effect on the fuel lubricity in comparison to the sunflower oil and cotton seed oil diisopropanolamides. This could be attributed to the high concentration of linoleic acid diisopropanolamide.

Figure 7. Impact of used frying oil diisopropanolamides addition on the lubrication properties of the base fuel.
Although all types of fatty acid diisopropanolamides tested in this series of experiments had a beneficial impact on the lubricity of marine gas oil, an interesting conclusion is derived from the comparison of fatty acid composition. Among the individual types of fatty acid diisopropanolamides, those derived from non-polyunsaturated oils such as olive oil and coconut oil appeared to have better lubrication performance. The higher lubricity effect can be attributed to the higher amount of saturated and mono-unsaturated diisopropanolamides. The basic mechanism is that the saturated compounds align in straight chains and closely crowd on the surface, providing a robust lubricating layer. When double bonds are present, the above mechanism does not take place, with the opposite results [27,28].

4. Conclusions

In an effort to investigate the impact of fatty acid diisopropanolamides on the tribological properties of low-sulfur marine fuel, seven mixtures of diisopropanolamides that were synthesized from various vegetable oils (sunflower oil, soybean oil, cotton seed oil, olive oil, tobacco seed oil, coconut oil, used frying oil) were added to a marine gas oil. The following conclusions can be drawn from this study:

- The low-sulfur marine gas oil does not provide satisfactory lubrication and may lead to damage in the fuel pumps of the marine diesel engines.
- It was proved that concentration levels of the fatty acid diisopropanolamides from 60 to 120 ppm decrease the initial wear scar diameter value of the base fuel within the acceptable requirement of 520 μm.
- Extra addition of amides did not provide additional improvement in the lubricity of the fuels.
- Among the individual types of fatty acid diisopropanolamides, those derived from non-polyunsaturated oils such as olive oil and coconut oil appear to be better lubricants.

Author Contributions: George Anastopoulos, Stamatios Kaligeros, Dimitrios Karonis and Fanourios Zannikos conceived and designed the experiments. Ypatia Zannikou and Petros Schinas performed the experiments. George Anastopoulos and Stamatios Kaligeros analyzed the data and wrote the paper.

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