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Impact of *N*,*N*-Bis(2-ethoxyethyl) Fatty Acid Amides on the Lubrication Performance of Kerosene Fuel F-34 for Use in CI Engines

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Abstract: In an attempt to avoid serious problems that can affect the efficiency of refueling ground-operated vehicles and aircraft during military operations, the Armed Forces of the North Atlantic Treaty Organization (NATO) are introducing the use of a unique fuel for both air and land use. The fuel that has been selected is the F-34, similar to Jet A-1, which is used in civil aviation, in order to replace diesel fuel in many applications. It has to be mentioned that tests performed with this fuel, which is kerosene type on the high frequency reciprocating rig (HFRR) have shown that such fuel is responsible for severe wear. This very high wear is related to the very low lubricity of aviation fuel. Having the idea to improve the lubricity of aviation fuel to the level of fuels used in compression ignition engines (diesel fuel), seven *N*,*N*-Bis(2-ethoxyethyl) fatty acid amides were formulated from various vegetable oils (sunflower oil, soybean oil, cottonseed oil, olive oil, tobacco seed oil, coconut oil, used frying oil), and they were evaluated as lubricity improvers of the aviation fuel. The required tribological measurements for lubricity rating were carried out by employing ISO 12156-1 test method on an HFRR instrument. The test conditions during the measurements were in the range of 55% to 58% for the relative humidity and 24 °C for the temperature. The results from the tribological measurements showed that all *N*,*N*-Bis(2-ethoxyethyl) fatty acid amides used were rated as efficient in order to provide an acceptable mean wear scar diameter (below 460 μm) at concentrations from 150 to 300 ppm. Additive concentrations below 150 ppm did not improve the lubricity at the required level. The increase of *N*,*N*-Bis(2-ethoxyethyl) fatty acid amides at concentrations over 300 ppm did not have any significant decrease in the wear scar diameter. A comparison between the *N*,*N*-Bis(2-ethoxyethyl) fatty acid amides showed that those formulated by non-polyunsaturated oils like olive oil and coconut oil seem to have better lubricity improver characteristics.

Keywords: lubricity; kerosene fuel; lubricating additives; fatty acid amides; HFRR

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1. Introduction

The implementation of jet propulsion engines in the U.S. Air Force fleet was accompanied by the introduction of the first aviation fuel, which was a "wide-cut" fuel, which is a hydrocarbon mixture within the boiling range of heavy gasoline and kerosene. The need to proceed to the implementation of single fuel for military use, especially in the case of operations, became imperative mainly for reasons of simplification in the supply chain. This transition took place in the 1970s when NATO air forces agreed and virtually completed the process of converting from the F-40 wide-cut fuel (JP-4) to a more safe and less flammable F-34 fuel, which is mainly kerosene-type fuel (F-34 is also known as JP-8 or

AVTUR/FSII). This change was largely based on the experience of the United States from its engagement in the Vietnam War [1].

The requirements for the operation and maintenance of NATO's extensive and costly pipeline network in times of peace, crisis, and conflict have led NATO member states to proceed with the implementation of a unique fuel (JP-8) for all air and land military assets and equipment when used on the European battlefield. This idea has been called the Single Fuel Concept (SFC) [2,3]. The fuel that has been chosen to implement the SFC is the F-34 (the military version of the kerosene type JP-8 fuel), which is similar to the civil aviation Jet A-1 fuel but includes also anti-icing, antistatic, and lubricity-improving additives. It may also contain antioxidant and metal-deactivator additives [4]. However, the findings of the research and the sufficient experience gained in peacetime were subsequently tested on the battlefield. A typical example is the sharp increase in the occurrence of infusion pump failures, due to the increased use of equipment, observed in Operation Desert Shield/Storm in 1990–1991 in Saudi Arabia [5,6]. From the experience gained, NATO considered it necessary to carry out further studies. Thus, the exchange of ideas and experiences between the member states of the alliance would reveal the areas of development and activities required for a better understanding of the engine performance when F-34 (JP-8) fuel was used, in order to solve the identified operational problems and failures [7,8].

It should be noted that a key problem was mentioned during the implementation steps of the single-fuel concept. Generally, the F-34 or the similar fuel F-35 was found to have lower lubricity than commercially available distillates in the diesel fuel range. A possible explanation is that diesel fuel contains longer hydrocarbon chains, (higher boiling range) compared to kerosene and has a higher amount of natural lubricating agents [8].

The main object of this work was to investigate the lubricating characteristics of kerosene-type JP-8 fuel with seven added *N*,*N*-Bis(2-ethoxyethyl) fatty acid amides. The tests that were performed, provided data to look up for the minimum concentration of the fatty acid amides, capable to provide mean wear scar diameter below 460 μm. The value of 460 mμ, which is widely accepted by the industry as a minimum requirement for acceptable performance on the field, has been proposed by the European Committee for Standardization (CEN) in 1997 [9]. This limit is used in the specifications of automotive diesel fuel in the European Union [10].

Fatty acids and their derivatives are significant additives that reduce friction (and wear) as they are oxygen-containing compounds [11–27]. The additives used as lubricity improvers contain a polar group that is attracted to the surfaces of the metal. This attraction has as result the formation of a thin surface film, which acts as a boundary lubricant between the metal surfaces. The addition of fatty acids [11,25], synthetic amide compounds [11], and biodiesel fuel [11,13,28] have been reported to enhance the lubricity of ultra-low sulfur diesel fuel as it is evaluated by the High Frequency Reciprocating Rig test. The improvement in fuel lubricity has been reported also for aviation turbine fuels when ester-type additives were used. Linear alkyl polar compounds have been proven effective when used as lubricity-improving additives in diesel fuels when they are used above a minimum level of 10–100 ppm [26,28]. Wei and Spikes have reported, that a significant improvement in lubricity was achieved by oxygen-containing compounds with phenolic-type or carboxylic acid groups. This improvement was recorded at a concentration of just a few parts per million [29]. It has been reported that the oxygen-carbon ratio (O/C) of fuel reduces particulate matter emissions (reduction to below 0.5 on the Bosch scale) when the O/C ratio is more than 0.2 [30–39].

Acid esters and amides have been extensively studied as lubricity enhancers for automotive diesel, but their efficiency on the lubricity of lower viscosity aviation fuels in order to be used in compression ignition engines has been limited evaluated.

2. Experimental Section

2.1. Materials

Sodium methoxide, *N*,*N*-Bis(2-ethoxyethyl) amine, and analytical reagents were supplied from Sigma Chemical Co.,(St. Louis, MS, USA) and they were of high grade. Sunflower oil, soybean oil, and olive oil were of market quality and they were purchased from a local grocery store. Cottonseed and coconut oil, non-commercially available, were obtained from Elin Verd Biofuels S.A. The waste frying oil was collected from local fast-food restaurants, and from the analysis, it was found to be a mixture of sunflower oil and olive oil. The tobacco seed oil, which was not commercially available was extracted from tobacco seeds on a laboratory scale. The procedure used for the extraction of tobacco seed oil was the following; the seeds were ground to a fine powder and then dried at 100 °C for 2 h. A Soxhlet extraction apparatus was used for the extraction from the seeds by hot hexane as extraction solvent, at a temperature of 65–70 °C. The extraction process lasted 4 h. At the end of the extraction process, the oil was separated from the hexane in a rotary evaporator under vacuum, and after that, it was dried at 60 °C and weighed. No further purification was used on the oils that were used. Table 1 gives their main quality characteristics. The kinematic viscosity of the vegetable oils ranges from 27 to 40 cSt. The oils that have the lowest value of kinematic viscosity at 40 °C were coconut oil and tobacco seed oil, while the oil with the highest value of kinematic viscosity at the same temperature is used frying oil.

The composition of fatty acids of the oils used in this study is given in Table 2. The fatty acid composition analysis showed that except for coconut oil, which contains a high amount of saturated fatty acids, the rest of the oils contain mainly (>70% m/m) unsaturated fatty acids. Olive oil and used frying oil contain high levels of mono-unsaturated fatty acids. For both oils, oleic acid is the major fatty acid, with concentrations of 75.0% m/m and 48.7% m/m, respectively. On the other hand, sunflower oil, soybean oil, cottonseed oil, and tobacco seed oil are clearly poly-unsaturated vegetable oils since they contain high amounts of linoleic acid. In addition, cottonseed oil had a significant amount of palmitic acid (22.2% m/m) compared to the other vegetable oils.

The scope of this study was to investigate the impact of the selected *N*,*N*-Bis(2-ethoxyethyl) fatty acid amides on the lubrication efficiency of kerosene type fuels, aviation fuel was provided by Hellenic Petroleum Elefsis Refinery, and it was used as the base fuel for all the tribological measurements. The main quality characteristics of the fuel are given in Table 3, with the standard test methods that were used for the measurement of the relevant properties.

Table 1. Main properties of vegetable oils with relevant measurement uncertainties.

Properties	Sunflower Oil	Soybean Oil	Olive Oil	Cottonseed Oil	Coconut Oil	Used Frying Oil	Tobacco Seed Oil	Test Method
Kinematic Viscosity at 40 °C (cSt)	32.6 ± 0.03	33.07 ± 0.03	29.4 ± 0.02	28.4 ± 0.02	27.3 ± 0.02	40.2 ± 0.03	27.7 ± 0.02	EN ISO 3104
Density at 15 °C (kg/m^3)	921.7 ± 0.08	918.6 ± 0.07	908.2 ± 0.06	914.8 ± 0.08	924.0 ± 0.08	926.0 ± 0.07	917.5 ± 0.06	EN ISO 12185
Flash Point (°C)	272 ± 3	246 ± 3	268 ± 3	234 ± 3	311 ± 3	286 ± 3	220 ± 3	EN 22719
Iodine Number (cg I_2/g oil)	132 ± 4	108 ± 3	100 ± 3	115 ± 3	53.5 ± 2	108 ± 3	135 ± 4	EN 14111
Acid Value (mg KOH/g)	0.33 ± 0.03	1.02 ± 0.07	0.25 ± 0.02	0.16 ± 0.02	0.22 ± 0.02	1.7 ± 0.08	0.48 ± 0.03	EN 14104
Saponification Value (mg KOH/g)	192.1 ± 0.5	170.4 ± 0.4	196.2 ± 0.5	190 ± 0.5	267.6 ± 1.1	193.2 ± 0.5	193.0 ± 0.5	AOCS CD3 1993
Water Content (mg/kg)	347 ± 0.5	512 ± 0.8	274 ± 0.5	578 ± 1.0	270 ± 0.5	933 ± 1.9	754 ± 0.15	EN ISO 12937
Sulfur Content (mg/kg)	0.23 ± 0.004	3.0 ± 0.04	2.6 ± 0.03	3.2 ± 0.03	2.7 ± 0.04	5.7 ± 0.05	8.2 ± 0.06	EN ISO 20846
Carbon Residue (% m/m)	0.031 ± 0.0004	0.056 ± 0.0008	0.092 ± 0.001	0.073 ± 0.0009	0.217 ± 0.02	0.181 ± 0.02	0.086 ± 0.01	EN ISO 10370

Table 2. Fatty acid composition of vegetable oils, % m/m with measurements uncertainties.

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)	$CH_3(CH_2)_{10}COOH$	0.0	0.1 ± 0.01	0.0	0.0	49.2 ± 0.02	2.0 ± 0.01	0.0
Myristic (C14)	$CH_3(CH_2)_{12}COOH$	0.0	0.1 ± 0.01	0.0	0.8 ± 0.01	18.5 ± 0.02	0.3 ± 0.01	0.1 ± 0.01
Palmitic (C16)	$CH_3(CH_2)_{14}COOH$	6.2 ± 0.01	11.3 ± 0.01	11.6 ± 0.01	22.2 ± 0.02	9.1 ± 0.02	15.7 ± 0.02	11.0 ± 0.02
Palmitoleic (C16:1)	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$	0.1 ± 0.01	0.0	0.9 ± 0.01	0.4 ± 0.01	0.1 ± 0.01	0.3 ± 0.01	0.2 ± 0.01
Stearic (C18)	$CH_3(CH_2)_{16}COOH$	3.7 ± 0.01	4.1 ± 0.01	3.1 ± 0.01	2.2 ± 0.01	2.7 ± 0.01	3.1 ± 0.01	3.3 ± 0.01
Oleic (C18:1)	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	25.2 ± 0.02	22.7 ± 0.02	75.0 ± 0.03	17.7 ± 0.02	6.5 ± 0.01	48.7 ± 0.02	15.5 ± 0.02
Linoleic (C18:2)	$CH_3(CH_2)_3(CH_2CH{=}CH)_2(CH_2)_7COOH$	63.1 ± 0.02	52.6 ± 0.02	7.8 ± 0.02	55.8 ± 0.02	1.7 ± 0.01	22.4 ± 0.02	69.5 ± 0.02
Linolenic (C18:3)	$CH_3(CH_2CH{=}CH)_3(CH_2)_7COOH$	0.3 ± 0.01	7.4 ± 0.02	0.6 ± 0.01	0.1 ± 0.01	0.0	1.0 ± 0.01	0.7 ± 0.01
Eicosenoic (C20)	$CH_3(CH_2)_8CH{=}CH(CH_2)_8COOH$	0.2 ± 0.01	0.5 ± 0.01	0.0	0.2 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.3 ± 0.01
Behenic (C22)	$CH_3(CH_2)_{20}COOH$	0.7 ± 0.01	0.5 ± 0.01	0.1 ± 0.01	0.0	0.1 ± 0.01	0.2 ± 0.01	0.1 ± 0.01
Erucic (C22:1)	$CH_3(CH_2)_7CH{=}CH(CH_2)_{11}COOH$	0.1 ± 0.01	0.2 ± 0.01	0.0	0.0	0.0	0.0	0.0
Lignoceric (C24)	$CH_3(CH_2)_{22}COOH$	0.2 ± 0.01	0.2 ± 0.01	0.5 ± 0.01	0.0	0.0	0.3 ± 0.01	0.0

Table 3. Main properties of aviation fuel with measurements uncertainties.

Properties	JP-8	Method
Density (kg/m^3, 15 °C)	795.0 ± 0.1	ASTM D 1298
Kinematic Viscosity (cSt, −20 °C)	3.87 ± 0.005	ASTM D 445
Flash Point (°C)	41 ± 0.5	ASTM D 93
Conductivity (pS/m)	375 ± 5	ASTM D 2624
Sulfur wt%	0.23 + 0.007	ASTM D 4294
Aromatics vol%	15.3 ± 0.6	ASTM D 1319
Olefins vol%	0.3 ± 0.1	ASTM D 1319
Lubricity		
Initial measurement, μm	754 ± 2	ISO 12156-1
Repeated measurement, μm	758 ± 2	
Distillation (°C)		
IBP	145 ± 2	
10%	174 ± 1	
20%	181 ± 1	ASTM D 86
50%	200 ± 1	
90%	233 ± 1	
FBP	250 ± 2	

2.2. Synthesis of N,N-Bis(2-ethoxyethyl) Fatty Acid Amides

The reaction was conducted in a glass reaction flask with a round bottom, which was submerged in an oil bath. The reaction equipment included a mechanical stirrer, thermometer, and condenser, in order to ensure proper mixing, temperature control, and reflux. *N*,*N*-Bis(2-ethoxyethyl) amine reacted with the oils at a stoichiometric ratio of (*N*,*N*-Bis(2-ethoxyethyl) amine oil with sodium methoxide (1.5% by mass of *N*,*N*-Bis(2-ethoxyethyl) amine and oil) as a catalyst. The reactions were conducted at 120 °C, and the formation of *N*,*N*-Bis(2-ethoxyethyl) fatty acid amides was checked by Thin Layer Chromatography. After the end of each reaction, the reaction mixture was left to cool at ambient temperature and later it was dissolved in diethyl ether in a separating funnel. The ether phase was washed to neutralize the alkalinity of the catalyst with 5% aqueous hydrochloric acid. The ether phase was separated, washed with water for neutralization, and dried passing over sodium sulfate. The ether was removed from the neutralized ether layer using a rotary evaporator. The reaction scheme is depicted in Figure 1.

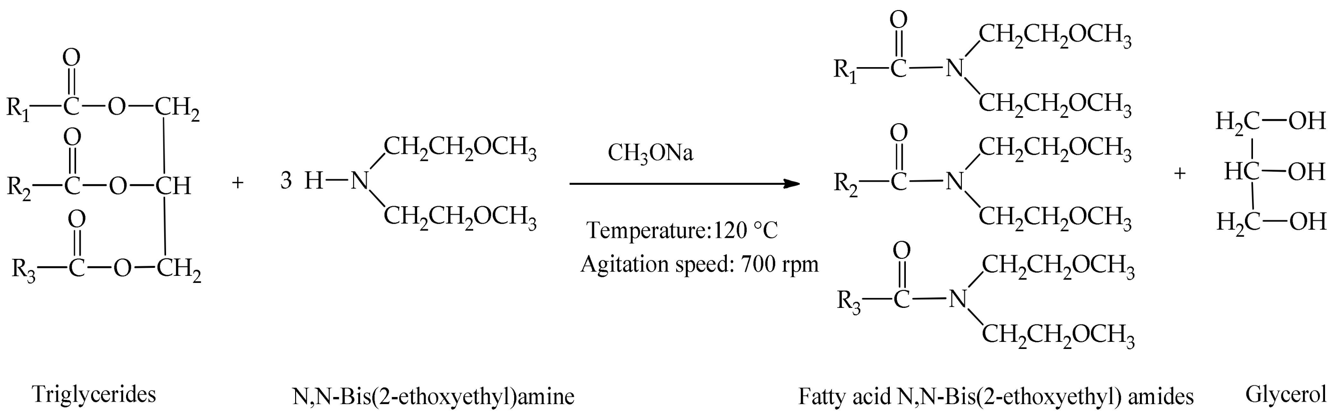

Figure 1. General reaction scheme for the synthesis of fatty acid *N*,*N*-Bis(2-ethoxyethyl) amides.

2.3. Tribological Measurements

The tribological measurements were carried out following the ISO 12156-1 method on the HFRR apparatus. In order to run the tests, a fuel volume of 2 mL was used, and the test temperature was 60 °C. The relative humidity was in the range of 55% to 58%, and the mean ambient temperature was 24 °C. The lubricating characteristics of all samples were rated by measuring the average wear scar diameter (WSD) of the spherical steel specimen.

A photomicroscope was used for the measurement of the WSD. The efficiency of the fuels to provide lubricity was rated by the measurement of the average wear scar diameter (WSD) of the spherical specimen by using a photomicroscope. The measured values of wear scars were corrected to provide WS 1.4 values, according to the requirements of the test method. The following equation was used for the calculation of the repeatability of the results [40]:

$$R = 139-(0.1648 \times WS1.4)$$

The seven *N*,*N*-Bis(2-ethoxyethyl) fatty acid amide mixtures were dissolved in the base fuel, at the same concentration levels, which were 50, 100, 150, 200, 250, 300, 350, and 400 ppm.

3. Results and Discussion

The initial step was the determination of the lubricity of the base fuel. The value of the corrected WSD for the base fuel, measured on the first day of its production, is given in Table 3. It is clear that the wear scar diameter of the fuel is much higher than 460 μm, which is the maximum acceptable limit for automotive fuel, and was therefore characterized as fuel with very poor lubricating characteristics. The repletion of the lubricity measurement on the next day gave an almost identical result and confirmed this remark. Due to the poor lubrication characteristics, this fuel was characterized as proper in the attempt to evaluate the lubricity effectiveness of the additives.

Figure 2 presents, in graphical form, the impact of the addition of the sunflower oil *N*,*N*-Bis(2-ethoxyethyl) amides on the corrected wear scar diameter of the base fuel. The addition of sunflower oil *N*,*N*-Bis(2-ethoxyethyl) amides at small concentrations, in the range of 50 to 200 ppm reduced the WS 1.4 of the base fuel, but not at the acceptable level. A substantial reduction of the wear scar diameter was shown when the dosage level of the sunflower oil *N*,*N*-Bis(2-ethoxyethyl) amides was increased to the level of 250 ppm. It is mentioned that the limit of 460 μm was not met, even in this case. When the concentration of sunflower oil *N*,*N*-Bis(2-ethoxyethyl) amides was increased from 250 to 300 ppm, a further reduction of WS 1.4 by 40 μm was measured, providing thus an improvement of the lubrication characteristics of the vase fuel at an acceptable level. When the concentration of sunflower oil *N*,*N*-Bis(2-ethoxyethyl) amides was between 300 and 400 ppm the reduction of WS 1.4 values was insignificant, and the fuel had an almost stable value of wear scar diameter at about 442 μm.

The efficiency of soybean oil *N*,*N*-Bis(2-ethoxyethyl) amides on the lubricating characteristics of the base fuel is presented in Figure 3. From the analysis of the results, it is shown that when soybean oil *N*,*N*-Bis(2-ethoxyethyl) amides were added in concentrations between 50 and 250 ppm even though it improved the lubrication characteristics of the base fuel, it did not approach the required value of 460 μm. The lubricity improvement at an acceptable level took place when the concentration of soybean oil *N*,*N*-Bis(2-ethoxyethyl) amides was increased from 250 to 300 ppm, where the maximum acceptable wear scar diameter of 460 μm measured by the HFRR, mandatory for commercial diesel fuels was achieved.

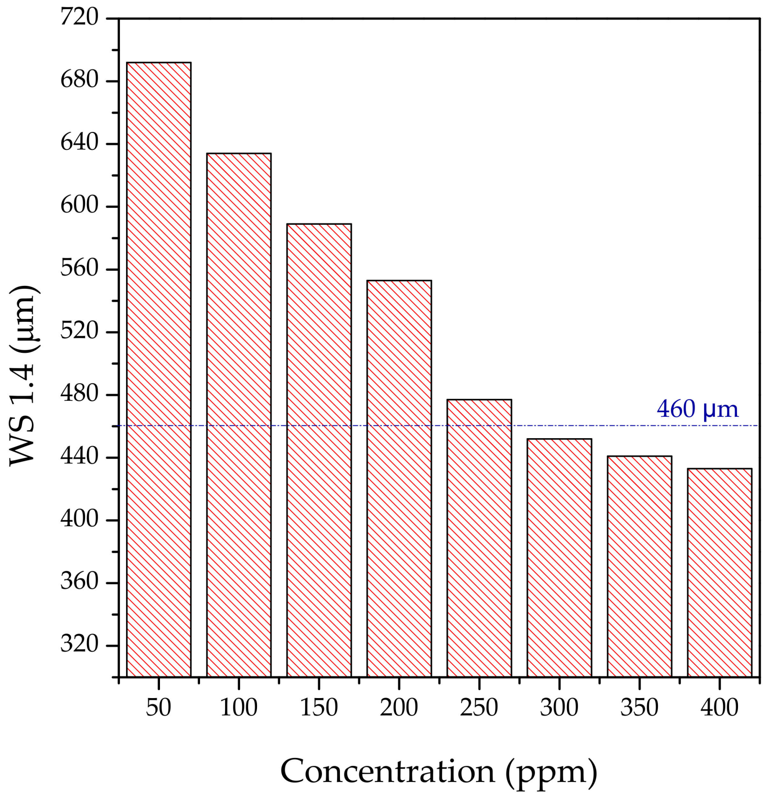

Figure 2. Impact of sunflower oil *N*,*N*-Bis(2-ethoxyethyl) amides addition on the lubrication characteristics of the base fuel.

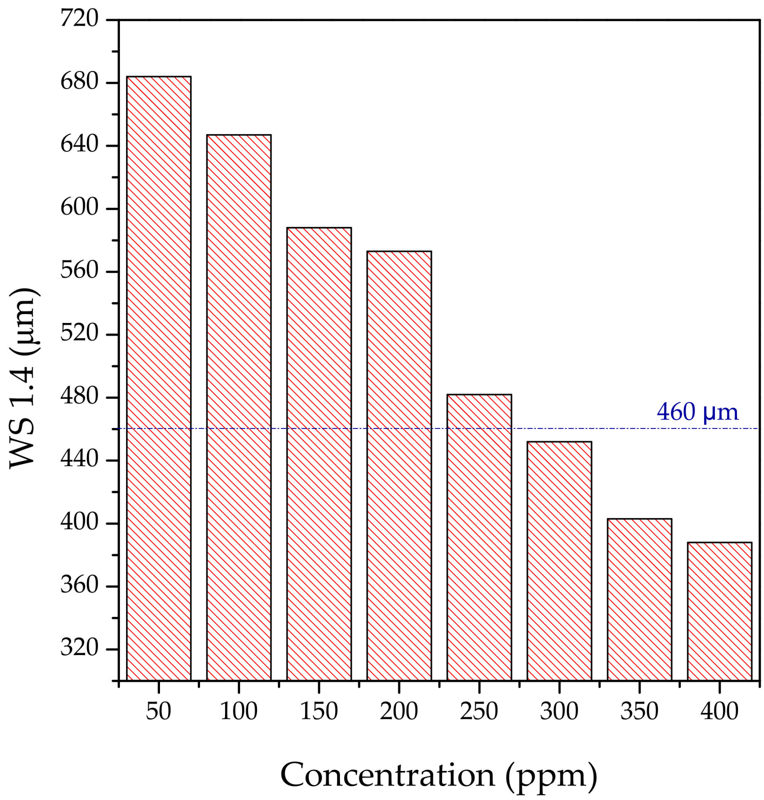

Figure 3. Impact of soybean oil *N*,*N*-Bis(2-ethoxyethyl) amides addition on the lubrication characteristics of the base fuel.

Figure 4 presents, the impact of the addition of *N*,*N*-Bis(2-ethoxyethyl) amides derived from olive oil on the lubricity of the base fuel. Based on the results from the HFRR, it can be seen that the addition of olive oil *N*,*N*-Bis(2-ethoxyethyl) amides at dosage levels below 200 ppm does not improve the lubrication characteristics of the base fuel to the required level. An increase of olive oil *N*,*N*-Bis(2-ethoxyethyl) amides mixture concentration at 200 ppm achieved a further reduction on the WS 1.4 to below the acceptance limit of 460 µm. The addition of an extra amount of *N*,*N*-Bis(2-ethoxyethyl) amides improves even better the lubrication characteristics of the base fuel. A further increase of olive oil amides concentration to 250 and 300 ppm, resulted in a reduction of the wear scar diameter at the value of 388 µm. The comparison of the tribological results determined from the addition of olive oil *N*,*N*-Bis(2-ethoxyethyl) amides on the base fuel, with the results from the addition of amides derived from sunflower oil *N*,*N*-Bis(2-ethoxyethyl), shows clearly that the olive oil *N*,*N*-Bis(2-ethoxyethyl) amides have significantly higher performance on the lubrication properties of the base fuel, which may be explained by the high content of mono-unsaturated *N*,*N*-Bis(2-ethoxyethyl) amides (mainly oleic acid amides), even at the lowest concentration of *N*,*N*-Bis(2-ethoxyethyl) palmitic acid amide of.

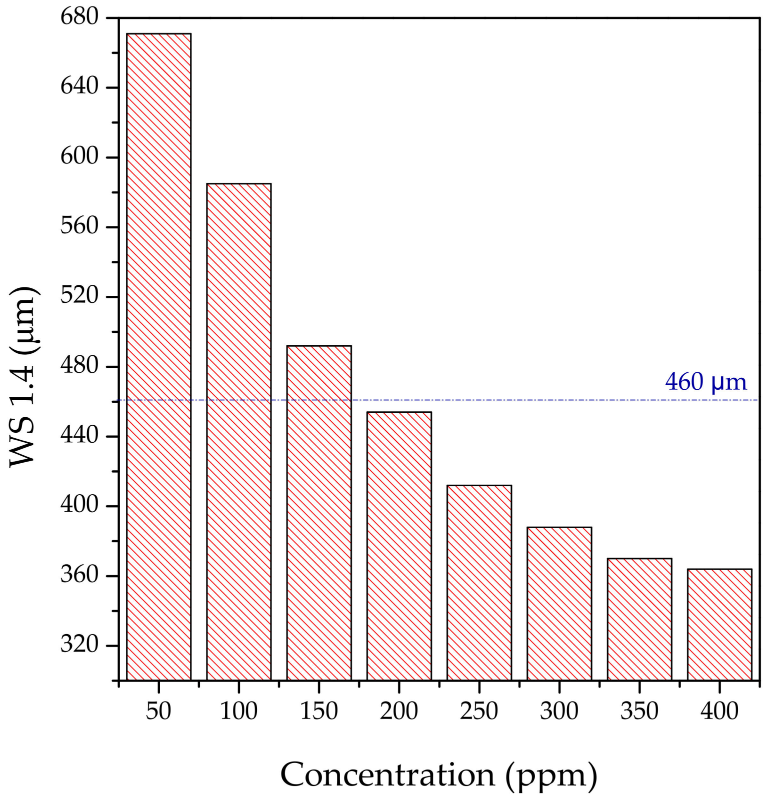

Figure 4. Impact of olive oil *N*,*N*-Bis(2-ethoxyethyl) amides addition on the lubrication characteristics of the base fuel.

Figure 5 presents the impact of the cottonseed oil *N*,*N*-Bis(2-ethoxyethyl) amides addition on the lubrication properties of the base fuel. Similar to the case of sunflower oil *N*,*N*-Bis(2-ethoxyethyl) amides, shown in Figure 2, in this case, the required dosage in order to achieve an acceptable wear scar diameter at the level of 460 µm was 300 ppm. A higher concentration of the cottonseed oil *N*,*N*-Bis(2-ethoxyethyl) amides increased only slightly the fuel lubricity. A closer look at the experimental results shows that cottonseed oil *N*,*N*-Bis(2-ethoxyethyl) amides have a slightly better lubrication efficiency compared to sunflower oil *N*,*N*-Bis(2-ethoxyethyl) amides. Even though both types of *N*,*N*-Bis(2-ethoxyethyl) amides achieve the required level of lubricity at a concentration of 300 ppm, at this dosage level, the WSD of sunflower oil *N*,*N*-Bis(2-ethoxyethyl) amides was 452 μm, while the relevant WSD value of *N*,*N*-Bis(2-ethoxyethyl) amides of the cottonseed oil was 389 μm. Therefore, the cottonseed oil *N*,*N*-Bis(2-ethoxyethyl) amides had a slightly better lubrication efficiency. A possible explanation for this remark can be attributed to the fact that cottonseed oil *N*,*N*-Bis(2-ethoxyethyl) amides contain more palmitic acid *N*,*N*-Bis(2-ethoxyethyl) amide compared to sunflower oil *N*,*N*-Bis(2-ethoxyethyl) amides. As a consequence, the slightly better lubrication performance of cottonseed oil *N*,*N*-Bis(2-ethoxyethyl) amides, is possibly explained by the presence of saturated fatty acids in higher content.

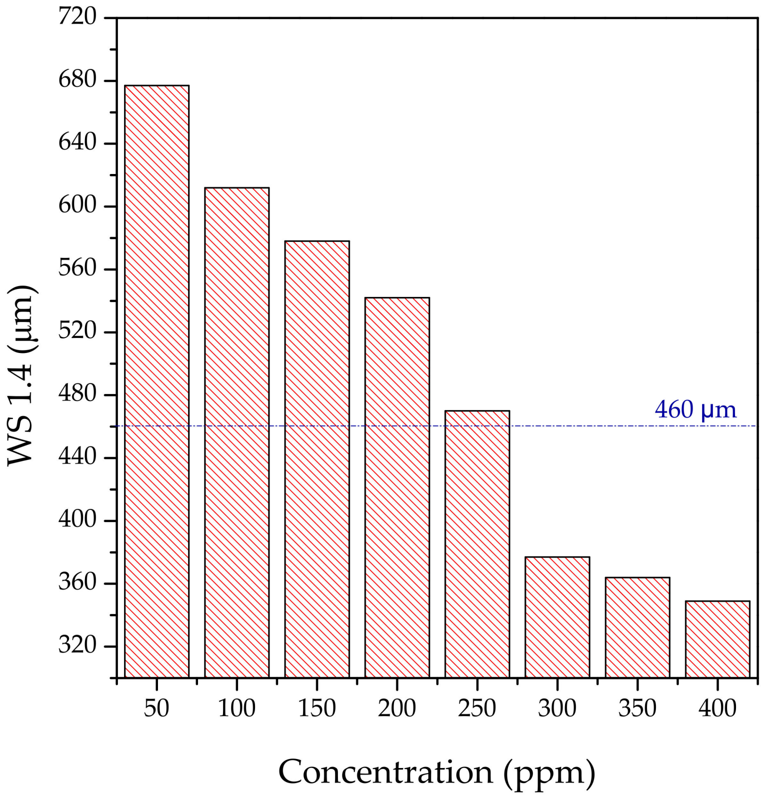

Figure 5. Impact of cottonseed oil *N*,*N*-Bis(2-ethoxyethyl) amides addition on the lubrication characteristics of the base fuel.

Figure 6 depicts, the impact of the addition of coconut oil *N*,*N*-Bis(2-ethoxyethyl) amides on the lubrication characteristics of the base fuel. The addition of coconut oil *N*,*N*-Bis(2-ethoxyethyl) amides at concentrations below 150 ppm did not improve the lubricity at the required level, however, a remarkable improvement in the lubricity was recorded when the *N*,*N*-Bis(2-ethoxyethyl) amides were used at a concentration of 150 ppm. At this treatment rate, WS 1.4 was decreased to 455 μm. It has to be mentioned that these fatty acid amides had the best impact on the lubricity of the base fuel in comparison with the other types of *N*,*N*-Bis(2-ethoxyethyl) amides that were examined. This observation supports the hypothesis that increasing the content of saturated and mono-unsaturated *N*,*N*-Bis(2-ethoxyethyl) amides also increases the lubrication efficiency.

Figure 7 presents the impact of the lubricity of the base fuel due to the addition of used frying oil *N*,*N*-Bis(2-ethoxyethyl) amides. From a first view, this particular type *N*,*N*-Bis(2-ethoxyethyl) amides improves the lubricating characteristics of the base fuel. When looking up the trend curve, it is shown that the acceptance limit of 460 μm for the WS 1.4 can be achieved at a treatment rate of *N*,*N*-Bis(2-ethoxyethyl) amides at 250 ppm or more. The comparison of the lubricity results of used frying oil *N*,*N*-Bis(2-ethoxyethyl) amides with the *N*,*N*-Bis(2-ethoxyethyl) amides that contain high levels of C18:2, it can be concluded that *N*,*N*-Bis(2-ethoxyethyl) amides of used frying oil have higher lubrication efficiency. The improved efficiency of this type of *N*,*N*-Bis(2-ethoxyethyl) amides on the lubrication characteristics of the fuel may be caused by the high content of both saturated and mono-saturated fatty acid *N*,*N*-Bis(2-ethoxyethyl) amides, which according to the results shown in Table 2, is about 70%.

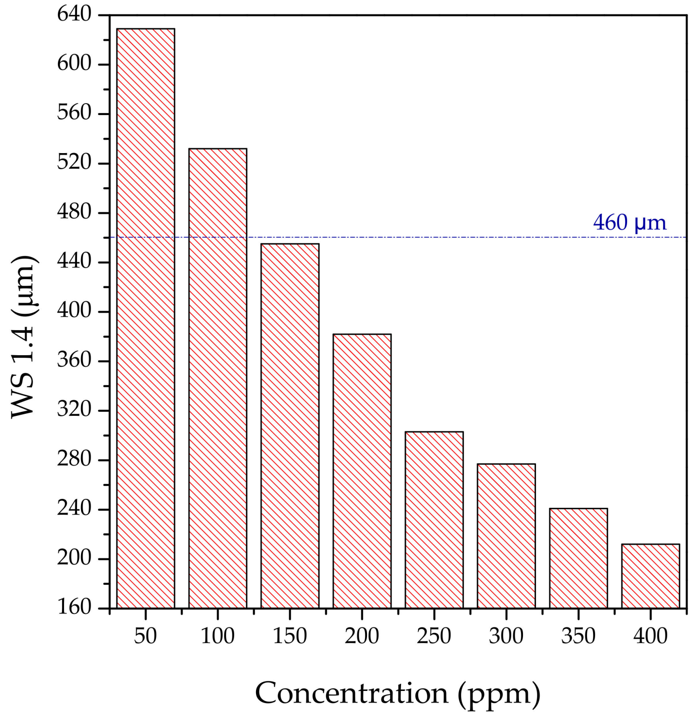

Figure 6. Impact of coconut oil *N*,*N*-Bis(2-ethoxyethyl) amides addition on the lubrication characteristics of the base fuel.

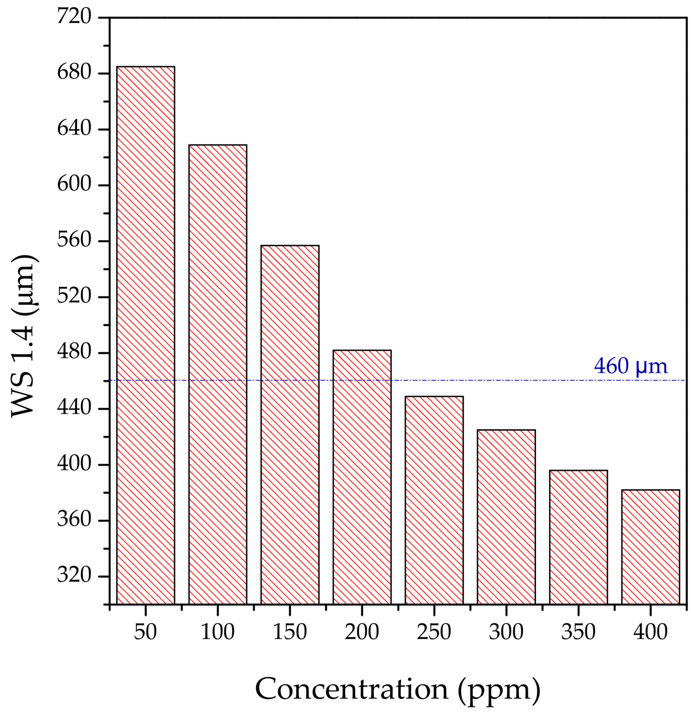

Figure 7. Impact of used frying oil *N*,*N*-Bis(2-ethoxyethyl) amides addition on the lubrication characteristics of the base fuel.

In Figure 8, the impact of the addition of tobacco seed oil *N*,*N*-Bis(2-ethoxyethyl) amides on the lubricity of the base fuel is shown. The *N*,*N*-Bis(2-ethoxyethyl) amides of the tobacco seed oil had similar behavior to those of cottonseed oil and sunflower oil *N*,*N*-Bis(2-ethoxyethyl) amides. In general, low dosage rates between 50 and 250 ppm did not have the desired impact on the lubricity of the base fuel. The desired decrease in WS 1.4 value was measured at the amide addition level of 300 ppm. Further increase in the dosage rate of tobacco seed oil *N*,*N*-Bis(2-ethoxyethyl) amides caused only a small increase in the WS 1.4 values. It must be mentioned that *N*,*N*-Bis(2-ethoxyethyl) amides of tobacco seed oil have a slightly worse impact on the lubricating characteristics of the base fuel compared to the *N*,*N*-Bis(2-ethoxyethyl) amides of cottonseed oil and sunflower oil. This worse behavior could be probably correlated with the high percentage of lineloic acid *N*,*N*-Bis(2-ethoxyethyl) amide in this case.

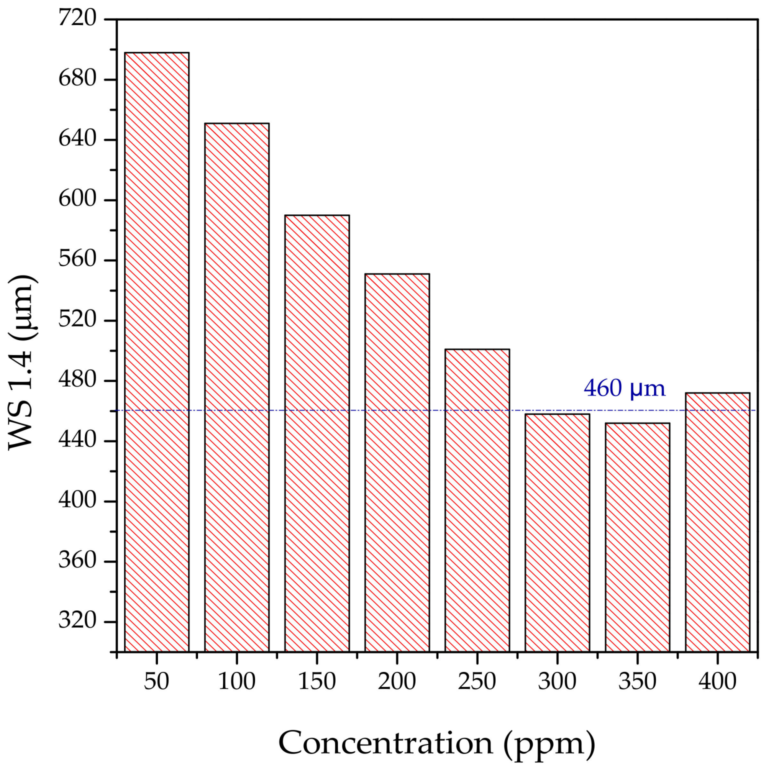

Figure 8. Impact of tobacco seed oil *N*,*N*-Bis(2-ethoxyethyl) amides addition on the lubrication characteristics of the base fuel.

From all the above results, it is clear that all types *N*,*N*-Bis(2-ethoxyethyl) amides of fatty acids tested in this experimental procedure, had a positive impact on the lubrication characteristics of a low-viscosity fuel in the range of kerosene. Apart from this remark, an interesting conclusion has been derived from the comparison of the fatty acid composition of the various oils used for the production of the amides. From the various types of fatty acid *N*,*N*-Bis(2-ethoxyethyl) amides, those synthesized from oils with low content of polyunsaturated oils, like olive oil and coconut oil were found to have better lubrication efficiency. The better impact on lubrication characteristics can be correlated to the higher amount of saturated and mono-unsaturated *N*,*N*-Bis(2-ethoxyethyl) amides. In the case of saturated compounds, the molecules can be easily aligned in straight chains and are packed more closely on the metal surface, providing in this way the protective strong lubricating layer [41,42]. On the other hand, in the case of polyunsaturated molecules, the double bonds do not allow rotation and force the chains to bend. This bending makes more difficult the adjustment of the molecules close to each other, resulting in the formation of a thinner and weaker lubricating layer [43,44].

4. Conclusions

In this series of experiments, the main goal was the investigation of fatty acid *N*,*N*-Bis(2-ethoxyethyl) amides on the tribological characteristics of kerosene, in order to be used as fuel for compression ignition engines. For this reason, seven mixtures of *N*,*N*-Bis(2-ethoxyethyl) amides were synthesized from various vegetable oils (olive oil, sunflower oil, soybean oil, cottonseed oil, tobacco seed oil, coconut oil, used frying oil) and they were added to a military aviation fuel JP-8. The main conclusions that can be extracted from this study are as follows:

- Aviation fuel of kerosene type, when used in land equipment and vehicles of the army in the implementation of the single fuel concept, is a fuel with poor lubrication properties that does not provide the necessary lubricity and may cause serious damage in the fuel pumps of the engines.
- The necessary dosage levels of the fatty acid *N*,*N*-Bis(2-ethoxyethyl) amides, in order to decrease the wear scar diameter below the maximum acceptable limit of 460 μm, were in the range of 150 to 300 ppm. Any further addition of amides did not provide any significant improvement in the lubricity of the base fuel.
- Among the individual types of fatty acid *N*,*N*-Bis(2-ethoxyethyl) amides, those derived from non-polyunsaturated oils, such as olive oil and coconut oil appear to be better lubricants.

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References

1. Arkoudeas, P.; Kalligeros, S.; Zannikos, F.; Anastopoulos, G.; Karonis, D.; Korres, D.; Lois, E. Study of using JP-8 aviation fuel and biodiesel in CI engines. *Energy Convers. Manag.* **2003**, *44*, 1013–1102. [CrossRef]
2. Korres, D.M.; Lois, E.; Karonis, D. Use of J-8 Aviation Fuel and Biodiesel on a Diesel Engine. *SAE Tech. Pap.* **2004**, *1*, 3033. [CrossRef]
3. Schihl, P.; Hoogterp-Decker, L. On the Ignition Behavior of JP-8 in Military Relevant Diesel Engines. *SAE Int. J. Engines* **2011**, *4*, 1–13. [CrossRef]
4. Schihl, P.; Decker-hoogterp, L.; Pence, K.; Leonard, K. On the Premixed Phase Combustion Behavior of JP-8 in a Military Relevant Single Cylinder Diesel Engine. *SAE Int. J. Engines* **2011**, *4*, 27–37. [CrossRef]
5. Walentynowicz, J. Methodology and Results of Testing an Impact of F-34 Fuel on the Engine Reliability. *SAE Tech. Pap.* **2020**, *1*, 2133. [CrossRef]
6. Karczewski, M. Evaluation of the diesel engine feed by unified battlefield fuel F-34/F-35 mixed with biocomponents. *Combust. Engines* **2019**, *178*, 240–246. [CrossRef]
7. Karczewski, M.; Szczęch, L. Influence of the F-34 unified battlefield fuel with bio components on usable parameters of the IC engine. *Eksploat. I Niezawodn. Maint. Reliab.* **2016**, *18*, 358–366. [CrossRef]

8. Hountalas, D.T.; Yfantis, E.; Papagiannakis, R.G.; Kotsiopoulos, P.N. Single Fuel Research Program Comparative Results of the Use of JP-8 Aviation Fuel versus Diesel Fuel on a Direct Injection and Indirect Injection Diesel Engine. *SAE Tech. Pap.* **2006**, *1*, 1673. [CrossRef]
9. European Committee for Standardization (CEN). Specification Automotive Diesel. In Proceedings of the 14th Meeting, Vienna, Austria, 6 February 1997.
10. *EN 590:2013+A1:2017*; Automotive fuels—Diesel—Requirements and test methods. European Committee for Standardization: Brussels, Belgium, 2017.
11. Anastopoulos, G.; Lois, E.; Serdari, A.; Zanikos, F.; Stournas, S.; Kalligeros, S. Lubrication properties of low-sulfur diesel fuels in the presence of specific types of fatty acid derivates. *Energy Fuels* **2001**, *15*, 106–112. [CrossRef]
12. Geller, D.P.; Goodrum, J.W. Effects of specific fatty acid methyl esters on diesel fuel lubricity. *Fuel* **2004**, *83*, 2351–2356. [CrossRef]
13. Knothe, G.; Steidley, K.R. Lubricity of components of biodiesel and petrodiesel. the origin of biodiesel lubricity. *Energy Fuels* **2005**, *19*, 1192–1200. [CrossRef]
14. Knothe, G. "Designer" biodiesel: Optimizing fatty ester composition to improve fuel properties. *Energy Fuels* **2008**, *22*, 1358–1364. [CrossRef]
15. Sulex, M.W.; Kulczycki, A.; Malysa, A. Assessment of lubricity of compositions of fuel oil with biocomponents derived from rape-seed. *Wear* **2010**, *268*, 104–108. [CrossRef]
16. Sukjit, E.; Dearn, K.D. Enhancing the lubricity of an environmentally friendly Swedish diesel fuel MK1. *Wear* **2011**, *271*, 1772–1777. [CrossRef]
17. Sukjit, E.; Tsolakis, A.; Dearn, K.D. Interrogating the surface: The effect of blended diesel fuels on lubricity. *SAE Int. J. Fuel Lubr. Technol.* **2012**, *5*, 154–162. [CrossRef]
18. Agarwal, S.; Chhibber, V.K.; Bhatnagar, A.K. Tribological behavior of diesel fuels and the effect of anti-wear additives. *Fuel* **2013**, *106*, 21–29. [CrossRef]
19. Loehle, S.; Matta, C.; Minfray, C.; Mogne, T.L.; Martin, J.M.; Iovine, R.; Obara, Y.; Miura, R.; Miyamoto, A. Mixed Lubrication with C18 Fatty Acids: Effect of Unsaturation. *Tribol. Lett.* **2014**, *53*, 319–328. [CrossRef]
20. Chong, W.W.F.; Ng, J.H. An atomic-scale approach for biodiesel boundary lubricity characterization. *Int. Biodeter. Biodegr.* **2016**, *113*, 34–43. [CrossRef]
21. Sundus, F.; Fazal, M.A.; Masjuki, H.H. Tribology with biodiesel: A study on enhancing biodiesel stability and its fuel properties. *Renew. Sust. Energ. Rev.* **2017**, *70*, 309–412. [CrossRef]
22. De Barros Bouchet, M.I.; Martin, J.M.; Forest, C.; le Mogne, T.; Mazarin, M.; Avila, J.; Asensio, M.C.; Fisher, G.L. Tribochemistry of unsaturated fatty acids as friction modifiers in (bio)diesel fuel. *RSC Adv.* **2017**, *7*, 33120–33131. [CrossRef]
23. De Oliveira, J.J.; Mendes de Farias, A.C.; Martins Alves, S. Evaluation of the biodiesel fuels lubricity using vibration signals and multiresolution analysis. *Tribol. Int.* **2017**, *109*, 104–113. [CrossRef]
24. Sukjit, E.; Poapongsakorn, P.; Dearn, K.D.; Lapuerta, M.; Sánchez-Valdepeñas, J. Investigation of the lubrication properties and tribological mechanisms of oxygenated compounds. *Wear* **2017**, *376*, 836–842. [CrossRef]
25. Sukjit, E.; Tongroon, M.; Chollacoop, N.; Yoshimura, Y.; Poapongsakorn, P.; Lapuerta, M.; Dearn, K.D. Improvement of the tribological behaviour of palm biodiesel via partial hydrogenation of unsaturated fatty acid methyl esters. *Wear* **2019**, *426*, 813–818. [CrossRef]
26. Kajdas, C.; Majzner, M. Boundary lubrication of low-sulphur diesel fuel in the presence of fatty acids. *Lubr. Sci.* **2001**, *14*, 83–108. [CrossRef]
27. Weinebeck, A.; Reinertz, O.; Murrenhoff, H. Boundary lubrication of biofuels and similar molecules. *SAE Int. J. Fuels Lubr.* **2017**, *10*, 645–651. [CrossRef]
28. Hu, J.B.; Du, Z.X.; Li, C.X.; Min, E. Study on the lubrication properties of biodiesel as fuel lubricity enhancers. *Fuel* **2005**, *84*, 1601–1606. [CrossRef]
29. Wei, D.; Spikes, H. The Lubricity of Diesel Fuels. *Wear* **1986**, *111*, 217–235. [CrossRef]
30. Patterson, J.; Hassan, M.; Clarke, A.; Shama, G.; Hellgardt, K.; Chen, R. Experimental Study of DI Diesel Engine Performance Using Three Different Biodiesel Fuels. *SAE Tech. Pap.* **2006**, *1*, 0234. [CrossRef]
31. Kotsiopoulos, P.; Papagiannakis, R.; Tsakalou, P.; Gazinou, I.; Yfantis, E. Experimental Investigation Concerning the Effect of the use of Biodiesel and F-34 (JP-8) Aviation Fuel on Performance and Emissions of a DI Diesel Engine. *SAE Tech. Pap.* **2007**, *1*, 1450. [CrossRef]
32. Dagaut, P.; Gaïl, S. Chemical kinetic study of the effect of a biofuel additive on Jet-A1 combustion. *J. Phys. Chem. A* **2007**, *111*, 3992–4000. [CrossRef]
33. Sukjit, E.; Herreros, J.M.; Dearn, K.D.; García-Contreras, R.; Tsolakis, A. The effect of the addition of individual methyl esters on the combustion and emissions of ethanol and butanol -diesel blends. *Energy* **2012**, *42*, 364–374. [CrossRef]
34. Sajjad, H.; Masjuki, H.H.; Varman, M.; Kalam, M.A.; Arbab, M.I.; Imtenan, S.; Ashrafur Rahman, S.M. Engine combustion, performance and emission characteristics of gas to liquid (GTL) fuels and its blends with diesel and bio-diesel. *Renew. Sust. Energ. Rev.* **2014**, *30*, 961–986. [CrossRef]
35. Nautiyal, P.; Subramanian, K.A.; Dastidar, M.G.; Kumar, A. Experimental assessment of performance, combustion and emissions of a compression ignition engine fuelled with Spirulina platensis biodiesel. *Energy* **2020**, *193*, 116861. [CrossRef]

36. Zhang, Z.; Jiaqiang, E.; Deng, Y.; Pham, M.; Zuo, W.; Peng, Q.; Yin, Z. Effects of fatty acid methyl esters proportion on combustion and emission characteristics of a biodiesel fueled marine diesel engine. *Energy Convers. Manag.* **2018**, *159*, 244–253. [CrossRef]
37. Ağbulut, Ü.; Sarıdemir, S.; Albayrak, S. Experimental investigation of combustion, performance and emission characteristics of a diesel engine fuelled with diesel–biodiesel–alcohol blends. *J. Braz. Soc. Mech. Sci. Eng.* **2019**, *41*, 1–12. [CrossRef]
38. Dugala, N.S.; Goindi, G.S.; Sharma, A. Experimental investigations on the performance and emissions characteristics of dual biodiesel blends on a varying compression ratio diesel engine. *SN Appl. Sci.* **2021**, *3*, 622. [CrossRef]
39. Chen, H.; Xie, B.; Ma, J.; Chen, Y. NOx emission of biodiesel compared to diesel: Higher or lower? *Appl. Therm. Eng.* **2018**, *137*, 584–593. [CrossRef]
40. *ISO 12156-1:2018*; Diesel fuel—Assessment of lubricity using the high-frequency reciprocating rig (HFRR)—Part 1: Test method. International Organization for Standardization: Geneva, Switzerland, 2018.
41. Bhuyan, S.; Sundararajan, S.; Yao, L.; Hammond, E.G.; Wang, T. Boundary lubrication properties of lipid-based compounds evaluated using microtribological methods. *Tribol. Lett.* **2006**, *22*, 2–11. [CrossRef]
42. Wadumesthrige, K.; Ara, M.; Salley, S.O.; Simon Ng, K.Y. Investigation of Lubricity Characteristics of Biodiesel in Petroleum and Synthetic Fuel. *Energy Fuels* **2009**, *23*, 2229–2234. [CrossRef]
43. Hong, F.T.; Alghamdi, N.M.; Bailey, A.S.; Khawajah, A.; Sarathy, S.M. Chemical and kinetic insights into fuel lubricity loss of low-sulfur diesel upon the addition of multiple oxygenated compounds. *Tribol. Int.* **2020**, *152*, 106559. [CrossRef]
44. Hu, Z.; Zhang, L.; Li, Y. Investigation of tall oil fatty acid as antiwear agent to improve the lubricity of ultra-low sulfur diesels. *Tribol. Int.* **2017**, *114*, 57–64. [CrossRef]