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Investigation of the lubrication properties and tribological mechanisms of oxygenated compounds

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Abstract: Lubrication properties and mechanisms of various oxygenated compounds were investigated. High-frequency reciprocating rig (HFRR) was applied to measure the lubricity. The effect of humidity, functional group, carbon-chain length, and unsaturation on the lubricity of the oxygenated compound were studied. After the lubricity test, microscopic observation of disc specimens was made in a scanning electron microscope (SEM). The functional moieties were found to be the factor that significantly influenced the lubricity and the sensitivity to humidity of the oxygenated compounds. Abrasive wear was the dominating mechanism for all of the oxygenated compounds. As the vapor pressure increased, wear became more severe due to the contribution of corrosion. While, chain length and unsaturation seemed to have an insignificant effect on lubricity of the fatty acid methyl ester.

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We confirm that, to our knowledge, all the claims, statements and conclusions are true and are our jointly held opinions.

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1	Investigation of lubrication properties and mechanisms of oxygenated compounds
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12 Abstract

Lubrication properties and mechanisms of various oxygenated compounds were 13 investigated. High-frequency reciprocating rig (HFRR) was applied to measure the lubricity. The 14 15 effect of humidity, functional group, carbon-chain length, and unsaturation on the lubricity of the oxygenated compound were studied. After the lubricity test, microscopic observation of disc 16 specimens was made in a scanning electron microscope (SEM). The functional moieties were 17 found to be the factor that significantly influenced the lubricity and the sensitivity to humidity of 18 the oxygenated compounds. Abrasive wear was the dominating mechanism for all of the 19 oxygenated compounds. As the vapor pressure increased, wear became more severe due to the 20 contribution of corrosion. While, chain length and unsaturation seemed to have an insignificant 21 effect on lubricity of the fatty acid methyl ester. 22

23 Keywords: Lubricity, Oxygenated compounds, Wear scar, Humidity.

1 **1. Introduction**

Several new technologies have been developed to increase the potential of fuel 2 combustion and decrease engine-out emissions in compression ignition engines. For example, 3 4 the common-rail systems achieve the high injection pressure to enhance the fuel atomization leading to better air mixing, faster fuel evaporation and more combustion efficiency. The water 5 injection to intake manifold can reduce the supercharged air temperature resulting a reduction in 6 NOx emissions without a large increase in PM emissions [1]. The production of high quality 7 refined fuel and synthetic fuel is another example successful to improve the engine performance 8 and exhaust gas emissions. However all technologies as mentioned challenge with the failure of 9 fuel injection equipment. Severely-loaded injector and pump of common-rail systems need fuels 10 with high lubricating capacity to avoid any tribological damaged surface problem on fuel 11 12 injection components. The existence of water in the air can significantly affect the lubricating properties of fuel and its effect is dependent on the fuel type and the applied load. A correlation 13 of increased wear scar with increased moisture content in the air was reported when aviation fuel 14 and diesel fuel were tested [2, 3]. The desulphurization process to limit sulfur content in diesel 15 fuel eliminates not only quantities of sulfur in diesel fuel but also those of lubricity-imparting 16 compounds such as polyaromatics and oxygen containing compounds leading to numerous fuel 17 injection equipment failures due to the rapid loss of fuel lubrication performance [4]. 18 Oxygenated compounds present in the fuel molecule play a key role on reducing exhaust gas 19 emissions, especially smoke and PM emissions, and their tribological behaviors of oxygenated 20 compounds are different due to polarity of each compound. The absence of polar compounds and 21 reactive species tend to form an oxide layer on the metallic surfaces but this oxide film can be 22 23 simply eliminated during rubbing process, as a result of producing relatively severe wear. The

presence of polar species which are preferentially adsorbed will prevent the formation of an oxide film [2, 5]. For reasons as stated the fuel lubricity is one of the most critical properties of convention fuels or alternative fuels to avoid severe contact condition in fuel injection equipment.

Many researches have been reported the use of additive or pure substances as blend 5 components to improve the lubricity of diesel fuel with low content of sulfur. Fatty acid and its 6 methyl ester are widely used as lubricity additive to enhance the lubricating properties of highly 7 refined fuel [6-8]. An increase in carbon-chain length of fatty acid esters tended to increase the 8 effectiveness of the boundary lubricant to reduce friction and wear [9, 10]. However there is no 9 clear trend between carbon-chain length of methyl esters and lubricity enhancing properties 10 when carbon number of 18 to 22 was tested [11]. Comparing the saturated and unsaturated 11 compounds of esters the molecules of saturated compounds can develop stronger lubricating 12 layer due to molecules are easier to align in straight chains and are more closely packed on the 13 surface, resulting in the better lubricity [12]. Conversely, a rough correlation between saturation 14 and lubricity enhancement showed that an increase in unsaturation will improve fuel lubricity, 15 when methyl ester of C_{18} series was investigated [11]. Biodiesels derived from several 16 feedstocks such as palm, rapeseed, soybean, castor and cotton seed have successfully been used 17 as diesel fuel lubricity enhancers and methyl ester of castor containing ricinoleic acid as main 18 composition showed a substantial improvement in lubricity when as little as 1% was added to 19 low sulfur diesel fuel [6]. The effect of functional group present in oxygenated compounds on 20 fuel lubricity was tested and the results showed that the capability to enhance the lubricity was 21 22 $COOH > CHO > OH > COOCH_3 > C=O > C-O-C$ [13].

According to the European and American standards of fuel lubricity, the high frequency reciprocating rig (HFRR) is widely employed as consequence of its ability to provide a wide range of wear mechanisms related with adhesive sliding wear, which is responsible for the fuel injection equipment failures [4]. The test methods require a steel ball sliding on a steel disc submerged in the fuel to form wear on specimens. In general, the wear scar on ball specimen is reported to classify the lubricity of fuels. The wear scars of 460 and 520 μm are the limits of diesel fuel lubricity prescribed by EN 590:2009 [14] and ASTM D 975 [15], respectively.

8 To consider the ambient temperature and the presence of water in the air (humidity) which significantly affects the fuel lubricity during the test [2], the European standard requires 9 that water vapor pressure lies within a specified range for the test, approximately 25%-65% 10 relative humidity at ambient air temperature of 25 °C. The average wear scar is corrected with 11 the factor as function of vapor pressure as called the humidity correction factor (HCF), leading to 12 final reported value of corrected wear scar (WS1.4). The HCF of 60 µm/kPa is proposed by the 13 standard for unknown chemical composition of the fuel. The recent work revealed that the HCF 14 is dependent on the chemical composition of fuel. It reported that an overestimation on corrected 15 wear scar diameters was observed for paraffinic fuels and alcohols when the standard humidity 16 correction factor was applied, while an underestimation was found in case of biodiesel fuels. The 17 HCF of 55 µm/kPa was proposed to normalize the wear scar of hydrocarbon fuels with carbon 18 number ranged from 10 to 20. The HCF of 70 µm/kPa was recommended for biodiesel fuel. The 19 HCF of 40 µm/kPa was suggested for alcohol fuel as practical value [16]. 20

In this work, the commercial diesel fuels, C_{10} oxygenated compounds and fatty acid methyl ester of C_9 - C_{18} were selected to evaluate the effect of the ambient air humidity on the wear scar so that specific humidity correction factors depending on the fuel composition used to normalize the wear scar diameter were proposed. In addition, worn surfaces of tested specimens
 were observed in a scanning electron microscope (SEM) and lubricity mechanisms of the
 oxygenated compounds were discussed.

4

5 2. Materials and methodology

6 2.1 Oxygenated compounds

The main characteristics of tested fuels and pure substances comprised of commercial diesel fuels and oxygenated compounds for the lubricity test are given in Table 1 [17-21]. The ultra-low sulphur diesel (ULSD) and biodiesel derived from rapeseed oil (RME) were provided by Shell Global Solutions UK. The ULSD was supplied with additives to keep the lubrication properties below the limitation required by EN 590. The C_{10} oxygenated compounds with different functional groups, selected methyl esters with carbon-chain length between C_9 - C_{18} and C_{18} methyl esters with variable unsaturation were purchased from Sigma-Aldrich.

14

15 2.2 Specimens

The standard test specimens are composed of two pieces, i.e. ball specimen and disc 16 specimen. Both ball and disc specimens are made of ANSI E-52100 steel. The chemical 17 composition of the ANSI E-52100 steel is shown in Table 2 [22]. However, the disc specimen 18 was prepared from annealed rod, while the ball specimen was hardened by quenching prior to 19 tempering [23]. Hardness and roughness of ball and disc specimens provided by the 20 manufacturer are summarized in Table 3. As the disc specimens will be used for an analysis of 21 wear mechanism after the test, the as-received disc specimen was etched and then investigated in 22 23 a scanning electron microscope (SEM). The microstructure of the as-received disc specimen was

shown in Figure 1. As a result of the annealing process, the disc specimen reveals spheroidized
 carbides dispersed in ferrite.

3

4 2.3 Lubricity test

5 The lubricity of tested fuels and pure substances were carried out in the high frequency reciprocating rig (HFRR). The parameters including the fuel temperature, fuel sample volume, 6 7 reciprocating frequency and stroke, test time and load weight were set according to the test methods specified in EN ISO 12156-1:2006 [24] and ASTM D 6079 standards [25]. The 8 temperature controlled cabinet and salt-water solutions were employed to obtain the different 9 conditions of air humidities during the test. The salts and the range of vapor pressures obtained 10 after the equilibrium of salts are described in Table 2. To evaluate the lubricity in term the mean 11 12 wear scar diameter (MWSD) the microscope with 100x magnification lens was used to measure the length of wear scar on the tested ball in the axis parallel and perpendicular to the sliding 13 direction. After the lubricity test, tested disc specimens were cleaned with acetone and then 14 investigated in a scanning electron microscope (SEM). 15

16

17 **2.4 Humidity correction factor (HFC)**

18 Regarding the EN ISO 12156-1 to consider the laboratory air condition during the
19 lubricity test, the mean wear scar diameter was calculated to the corrected wear scar diameter or
20 wear scar normalized to a vapor pressure of 1.4 kPa (WS1.4) as described in Equation (1):
21

22 WS1.4=MWSD+HCF(1.4-
$$p_v$$
) (1)

23

where p_v is the mean vapor pressure during the test and HCF is the humidity correction factor. The HCF can be determined by the differentiating equation 1 with respect to the vapor pressure shown the detail in equation 2 and the standard recommends the HCF value of 60 μ m/kPa for diesel fuel. From Table 5, the HCF of diesel fuel with low content of sulfur determined from the experimental data in this study is 57.70 μ m/kPa, which is comparable to the standard HFC value.

$$_{7} \text{ HCF} = \frac{\text{dMWSD}}{\text{dp}_{y}}$$
(2)

8

9 **3. Results and discussion**

10 **3.1 Effect of functional group**

Mean wear scar diameters (MWSDs) measured from specimens tested in various 11 oxygenated compounds at different vapor pressures and the normalized wear scar diameters (WS 12 1.4) for each oxygenated compound are shown in Figure 2 and 3, respectively. To obtain the 13 lubricity (WS 1.4) the HCF values of each compound calculated from linear fitting of results in 14 Figure 2 have been used. Lubricity of the oxygenated compounds decreased with increasing of 15 MWSD. As the oxygenated compounds contain different functional groups, the effect of 16 17 functional group enhancing lubricity can be listed as the following sequence: carboxyl > aldehyde > hydroxyl > ester > ether > ketone. The results corresponded with the previous studies 18 [26], except the results of carbonyl group which composed of ether and ketone. 19

The sizes of the wear scars optically observed on the disc specimens tested in various oxygenated compounds shown in Figure 4 display a similar trend comparing to the MWSD results (Figure 2). Generally, the lubricity of a fluid depends on its viscosity, i.e. fluid with high viscosity produces good boundary lubrication [27, 28]. Thus, in the cases of decanoic acid, decanal, and 1-decanol having relatively high viscosity (Table 1), small and smooth wear scars
were observed (Figure 4 (a)-(f)). However, 1-decanol, possessing the highest viscosity, yielded
comparatively larger wear scar, than decanoic acid and decanal. Therefore, viscosity was
unlikely the only factor influencing lubricity.

5 It was reported previously that lubricity of organic compounds mainly depends on their adsorption ability to a substrate [13]. Since the organic compounds usually attach to a substrate 6 7 via the functional moiety, the amount of organic compound molecules being able to adsorb on a substrate as well as the bonding strength between the organic compound and the substrate are 8 directly influenced the characteristic of the functional group. Cook and Hackerman found that 9 the organic compound with carboxyl group (COOH) could yield higher amount of molecules 10 adsorbed on steel than those with hydroxyl group did [29]. Moreover, due to the fact that 11 12 carboxyl group are more polar than other functional groups presenting in this study, it can form a stronger intermolecular bonding with a metal substrate [13]. Thus, decanoic acid composed of 13 carboxyl group resulted in the smallest and smoothest wear scars, i.e. the highest lubricity 14 (Figure 4 (a) and (b)). 15

In terms of polarity, carbonyl (C=O) and hydroxyl (OH) groups are ranked next to 16 carboxyl group. Therefore, decanal with carbonyl group and 1-decanol with hydroxyl group 17 produced larger wear scars (Figure 4 (c)-(f)), i.e. lower lubricity, than decanoic acid. Even 18 though 2-decanone was also composed of carbonyl group, its lubricity was the lowest (Figure 3). 19 Moreover, deep grooves were clearly observed on the disc specimens tested in 2-decanone 20 (Figure 4 (k) and (l)). Comparing with linear structure of decanal, the relatively branching chain 21 molecule of the 2-decanone prevents the chains to pack closely together and results in the weaker 22 23 lubricating layer. The same effect can be used to explain the lubrication of methyl nonanoate and

dipentyl ether having the branching structures. However, the adsorption of the chain molecule of
the compounds also depends on their molecular weight, i.e. increase in molecular weight leads to
increasing of adsorption ability on a substrate [30]. Therefore, methyl nonanoate and dipentyl
ether, having higher molecular weight comparing with 2-decanone, produced smaller and
smoother wear scars (Figure 4 (g)-(j)), i.e. the higher lubricity.

6

7 **3.2 Effect of humidity**

8 The effect of humidity on the lubricity of the oxygenated compounds was investigated by varying the vapor pressure in the test chamber. The results of MWSD at different vapor pressures 9 are shown in Figure 2. It is obvious that increase in vapor pressure led to increasing of MWSD. It 10 is likely that water from surrounding air could be absorbed into the oxygenated compound during 11 the test. As the viscosity of water is relatively low, the presence of water will reduce the overall 12 viscosity of the oxygenated compound. Thus, at higher vapor pressure, the water content in the 13 oxygenated compound became higher and resulted in decreasing of viscosity and lubricity of the 14 compound. Moreover, the existence of oxygen in water could lead to corrosion on metal 15 substrate which might contribute to destroy the lubricating film on the rubbing surface and 16 induce bigger wear scar [16]. 17

From Figure 2, the relationship between the MWSD and the vapor pressure is approximately linear and Equation (2) can be applied to calculated the slope of the linear-fitted curve, i.e. the humidity correction factor (HCF). The linear equations which best fitted the experimental results with the HCFs for different oxygenated compounds are summarized in Table 5. It can be seen that 2-decanone was very sensitive to the change in humidity as it has the highest HCF of 99.80 μm/kPa, while decanal was least sensitive to humidity with HFC of 13.46 μm/kPa. The sensitivity to humidity usually depends on the ability of the compound to absorb
 water from surrounding air, i.e. hygroscopy. Thus, it is likely that the functional group had
 significantly effect on hygroscopy of the oxygenated compound.

The close observation of worn surfaces was made in the SEM at high magnification 4 5 (Figure 5). Worn surface tested in decanal at low vapor pressure revealed quite smooth surface with insignificant grooves (Figure 5 (a)). On the other hand, the evidence of abrasive wear, i.e. 6 7 grooves, as well as material loss around carbide particles were clearly observed on the worn 8 surface from the test in decanal at high vapor pressure (Figure 5 (b)). Normally, ferrite is softer 9 and more active than carbide. Under corrosive environment, ferrite is likely to be corroded, 10 especially in the critical area, in this case, around carbide particles. Therefore, in the case of 11 decanal, as the vapor pressure increases abrasive wear with corrosion was likely the dominating 12 mechanism.

For specimens tested in methyl nonanoate and 2-decanone, since these compounds were quite sensitive to humidity, material loss could be observed even at low vapor pressure (Figure 5 (c) and (e)). In the case of methyl nonanoate, slightly deeper grooves were observed as the vapor pressure increased (Figure 5 (d)). However, for 2-decanone which is most sensitive to humidity, the worn surface tested at high vapor pressure revealed the severe abrasive wear with detachment of carbide particles from the surface (Figure 5 (f)).

19

20 **3.3 Effect of chain length and unsaturation**

The effect of chain length on lubricity was studied by varying the number of carbon atoms in fatty acid methyl ester (FAME) in the range of 12 to 18 carbon atoms as listed in Table 1. The MWSDs for the specimens tested in various types of FAME at different vapor pressures

1 are represented in Figure 6. The linear fitted equations and the HCFs for different FAMEs are also summarized in Table 6. It can be seen that HFCs did not change significantly as the number 2 of carbon atoms in the fatty acid chain changed. Unlike the effect of functional group, the 3 4 number of carbon atoms was not the factor influencing the sensitivity to humidity of the oxygenated compound. The corrected wear scars of the specimens tested in the FAMEs with 5 different chain lengths are shown in Figure 7. Since the increase of the chain length led to 6 increasing of lubricating film thickness [31], the boundary lubrication of the FAME tended to 7 increase slightly with increasing of carbon atoms in the fatty acid chain. The results also agreed 8 9 with the previous works [13], which suggested that the chain length had a minimum effect of lubricity. 10

Three types of FAMEs with different degrees of unsaturation were used in this study. The 11 FAMEs contain different numbers of double bond; methyl stearate (C18:0) contains no double 12 bond, methyl oleate (C18:1) contains one double bond, and methyl linoleate (C18:2) contains 13 two double bonds. The MWSDs of the three FAMEs are illustrated in Figure 8. As the most 14 unsaturated fatty acid, C18:2 was very sensitive to humidity, i.e. its HCF is the highest. The HFC 15 decreased with decrease in saturation of the fatty acid chain; the HFC of C18:2, C18:1, and 16 17 C18:0 are 108.02, 68.86, and 47.75 µm/kPa, respectively. Moreover, it can be seen in Table 5 that the HCF of rapeseed methyl ester (RME) is 85.80 µm/kPa. Since the RME is mainly 18 composed of C18:1 and C18:2 [32, 33], the contribution of each component affects the HFC 19 value of the RME. 20

The corrected wear scars of C18:0, C18:1, and C18:2 are shown in Figure 7. The lubricity of the FAME slightly decreased with increasing of unsaturation of fatty acid. However, it was found in the previous works that increase in unsaturation slightly improve the lubricity of fatty acid [34]. Therefore, it should be suggested that the effect of unsaturation on lubricity is trivial
 for the fatty acid.

3

4 **4.** Conclusion

In this study, effect of humidity on lubrication mechanisms of various oxygenated
compounds was investigated. The findings can be summarized as follows:

- The functional group significantly affects the lubricity of the oxygenated compounds.
 The effect of functional group enhancing lubricity can be listed as the following
 sequence: carboxyl > aldehyde > hydroxyl > ester > ether > ketone.
- The oxygenated compound with carboxyl group having the highest polarity could
 strongly adsorb on the metal surface and led to the highest lubricity. While, 2-decanone
 (ketone) has the lowest lubricity due to its relatively branching structure as well as low
 molecular weight which prevented the chain molecules from packing closely together.
- Lubricity of the oxygenated compounds decreased with increasing of vapor pressure. The sensitivity the oxygenated compounds to humidity was influenced by the functional group. In this study, ketone is most sensitive to the change in humidity, while aldehyde is least sensitive to the change in humidity.
- Both chain length and unsaturation of the fatty acid methyl ester have insignificant effect
 on the lubricity. However, the unsaturation could influence the sensitivity to humidity,
 i.e. unsaturated fatty acid was more sensitive to humidity that the saturated fatty acid.
- 21

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3

4 **References**

- [1] X. Tauzia, A. Maiboom, S.R. Shah, Experimental study of inlet manifold water injection on
 combustion and emissions of an automotive direct injection Diesel engine, Energy, 35
 (2010) 3628-3639.
- 8 [2] P.I. Lacey, Wear with low-lubricity fuels I. Development of a wear mapping technique,
 9 Wear, 160 (1993) 325-332.
- [3] P.I. Lacey, Evaluation of Oxidative Corrosion in Diesel Fuel Lubricated Contacts, Tribology
 Transactions, 37 (1994) 253-260.
- 12 [4] D.P. Wei, H.A. Spikes, The lubricity of diesel fuels, Wear, 111 (1986) 217-235.
- [5] J.K. Lancaster, A review of the influence of environmental humidity and water on friction,
 lubrication and wear, Tribology International, 23 (1990) 371-389.
- [6] D.P. Geller, J.W. Goodrum, Effects of specific fatty acid methyl esters on diesel fuel
 lubricity, Fuel, 83 (2004) 2351-2356.
- [7] J. Hu, Z. Du, C. Li, E. Min, Study on the lubrication properties of biodiesel as fuel lubricity
 enhancers, Fuel, 84 (2005) 1601-1606.
- [8] G. Knothe, "Designer" biodiesel: Optimizing fatty ester composition to improve fuel
 properties Energ Fuel, 22 (2008) 1358-1364.
- [9] G. Anastopoulos, E. Lois, F. Zannikos, S. Kalligeros, C. Teas, Influence of aceto acetic esters
 and di-carboxylic acid esters on diesel fuel lubricity, Tribol Int, 34 (2001) 749-755.
- [10] S. Bhuyan, S. Sundararajan, L. Yao, E.G. Hammond, T. Wang, Boundary lubrication
 properties of lipid-based compounds evaluated using microtribological methods, Tribology
 Letters, 22 (2006) 167-172.
- [11] J.W. Goodrum, D.P. Geller, Influence of fatty acid methyl esters from hydroxylated
 vegetable oils on diesel fuel lubricity, Bioresource Technol, 96 (2005) 851-855.
- [12] K. Wadumesthrige, M. Ara, S.O. Salley, K.Y. Simon Ng, Investigation of lubricity
 characteristics of biodiesel in petroleum and synthetic fuel, Energ Fuel, 23 (2009) 2229 2234.
- [13] G. Knothe, K.R. Steidley, Lubricity of components of biodiesel and petrodiesel: The origin
 of biodiesel lubricity, Energ Fuel, 19 (2005) 1192-1200.
- [14] EN 590, Automotive fuels-diesel requirement and test method, European committee for
 standardization. Brussels, Belgium, (2009).
- [15] ASTM D 975, Standard specification for diesel fuel oils, ASTM International, West
 Conshohocken, United States.
- [16] M. Lapuerta, J. Sánchez-Valdepeñas, E. Sukjit, Effect of ambient humidity and hygroscopy
 on the lubricity of diesel fuels, Wear, 309 (2014) 200-207.
- 39 [17] Sigma Aldrich Corporation.
- [18] H. Djojoputro, S. Ismadji, Density and Viscosity of Several Aldehydes Fragrance
 Compounds in Their Binary Mixtures with Ethanol at (298.15 K, 308.15 K, and 318.15 K),
- 42 Journal of Chemical & Engineering Data, 50 (2005) 2003-2007.

- [19] G. Knothe, K.R. Steidley, Kinematic viscosity of biodiesel fuel components and related
 compounds. Influence of compound structure and comparison to petrodiesel fuel
 components, Fuel, 84 (2005) 1059-1065.
- [20] M. Lapuerta, J. Rodríguez-Fernández, O. Armas, Correlation for the estimation of the density of fatty acid esters fuels and its implications. A proposed Biodiesel Cetane Index, Chemistry and Physics of Lipids, 163 (2010) 720-727.
- [21] E. Sukjit, J.M. Herreros, K.D. Dearn, R. García-Contreras, A. Tsolakis, The effect of the addition of individual methyl esters on the combustion and emissions of ethanol and butanol
 -diesel blends, Energy, 42 (2012) 364-374.
- [22] ASM Handbook, Volume 01 Properties and Selection: Irons, Steels, and High Performance Alloys, ASM International., Materials Park, OH, 1990.
- 12 [23] PCS Instruments, Datasheet: HFRR Specimens, PCS Instruments, London.
- [24] EN ISO 12156-1, Diesel fuel: Assessment of lubricity using the high frequency
 reciprocating rig (HFRR) Part 1: Test method, European committee for standardization,
 Brussel, Belgium, Part 1: Test method, (2008).
- [25] ASTM D 6079, Standard test method for evaluating lubricity of diesel fuels by the high
 frequency reciprocating rig (HFRR), ASTM international, West Conshohocken, United
 States.
- [26] G. Knothe, Dependence of biodiesel fuel properties on the structure of fatty acid alkyl
 esters, Fuel Process Technol, 86 (2005) 1059-1070.
- [27] N. Canter, Special Report: Boundary Lubricity Additives, Tribology and Lubrication
 Technology Magazine, 2009, pp. 10-18.
- [28] J. Luo, S. Wen, P. Huang, Thin film lubrication. Part I. Study on the transition between
 EHL and thin film lubrication using a relative optical interference intensity technique, Wear,
 194 (1996) 107-115.
- [29] E.L. Cook, N. Hackerman, Adsorption of Polar Organic Compounds on Steel, The Journal
 of Physical Chemistry, 55 (1951) 549-557.
- [30] M. Lapuerta, R. García-Contreras, J. Campos-Fernández, M.P. Dorado, Stability, lubricity,
 viscosity, and cold-flow properties of alcohol-diesel blends, Energ Fuel, 24 (2010) 4497 4502.
- [31] B.J. Bornong, P. Martin, Adsorption of polar organic molecules on chromium, The Journal
 of Physical Chemistry, 71 (1967) 3731-3736.
- [32] E. Sukjit, K.D. Dearn, Enhancing the lubricity of an environmentally friendly Swedish diesel fuel MK1, Wear, 271 (2011) 1772-1777.
- [33] E. Sukjit, K.D. Dearn, A. Tsolakis, Interrogating the surface: the effect of blended diesel
 fuels on lubricity, SAE Paper, (2011).
- [34] M. Lapuerta, J. Sánchez-Valdepeñas, D. Bolonio, E. Sukjit, Effect of fatty acid composition
 of methyl and ethyl esters on the lubricity at different humidities, Fuel, 184 (2016) 202-210.
- 39 40

- 1 Captions
- 2 Figure 1 Microstructure of the as-received disc specimen.
- 3 Figure 2 MWSD of oxygenated compounds.
- 4 Figure 3 Normalized wear scar of oxygenated compounds.
- 5 Figure 4 Wear scars on disc specimen tested in different oxygenated compounds.
- 6 Figure 5 Wear scars on disc specimen tested in different oxygenated compounds at high
- 7 magnification.
- 8 Figure 6 MWSD of FAMEs.
- 9 Figure 7 Effect of unsaturation of C18 FAMEs on MWSD.
- 10 Figure 8 Normalized wear scar of FAMEs.
- 11
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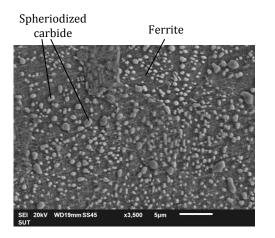


Figure 1 Microstructure of the as-received disc specimen.

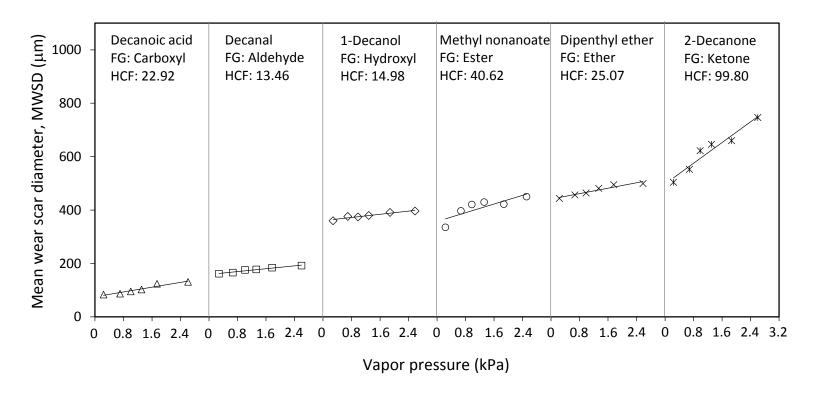


Figure 2 MWSD of oxygenated compounds.

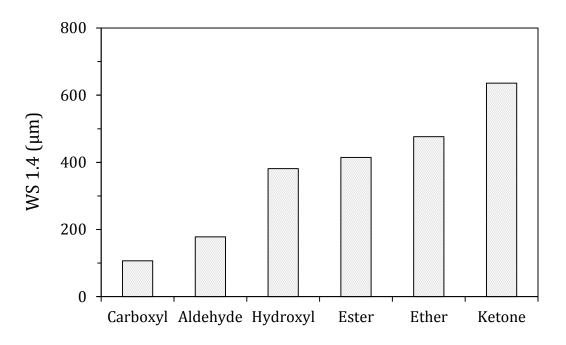
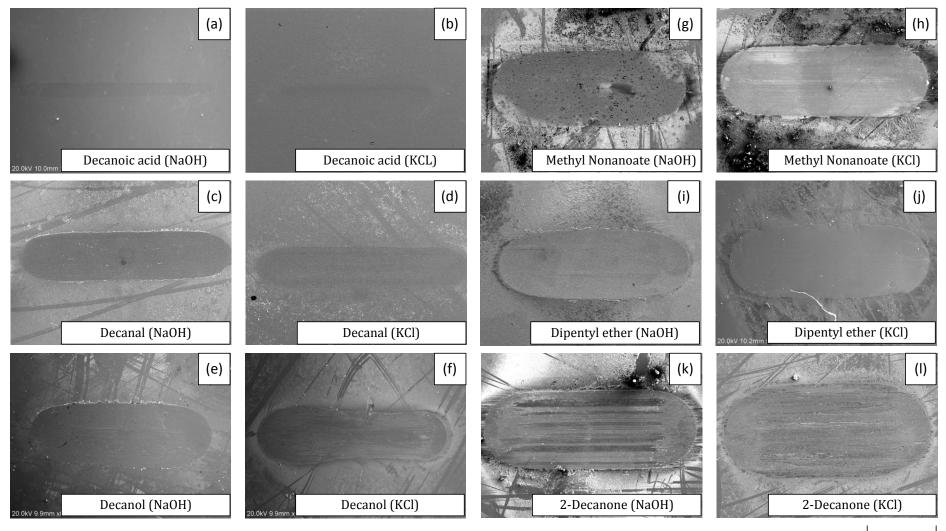


Figure 3 Normalized wear scar of oxygenated compounds.



500 µm

Figure 4 Wear scars on disc specimen tested in different oxygenated compounds.

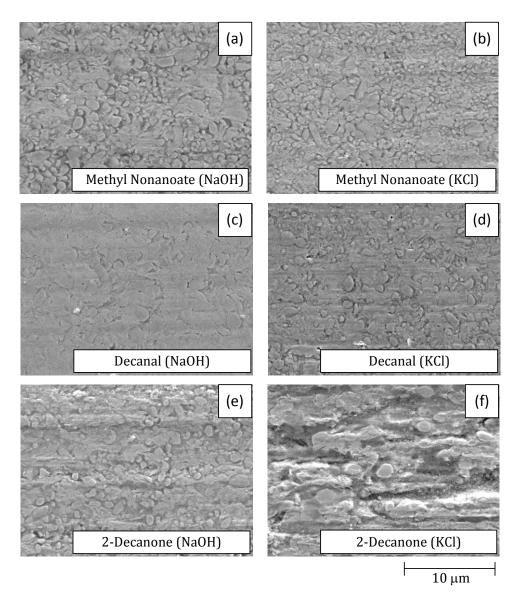


Figure 5 Wear scars on disc specimen tested in different oxygenated compounds at high magnification.

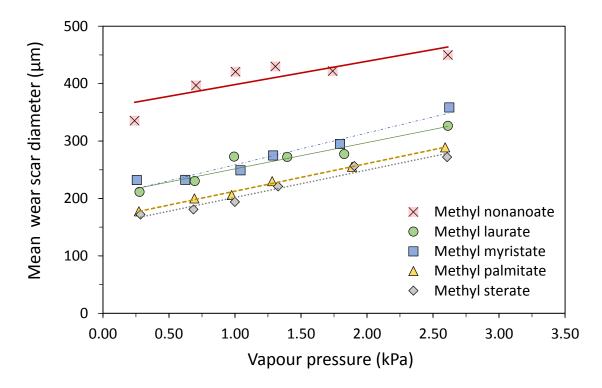


Figure 6 MWSD of FAMEs.

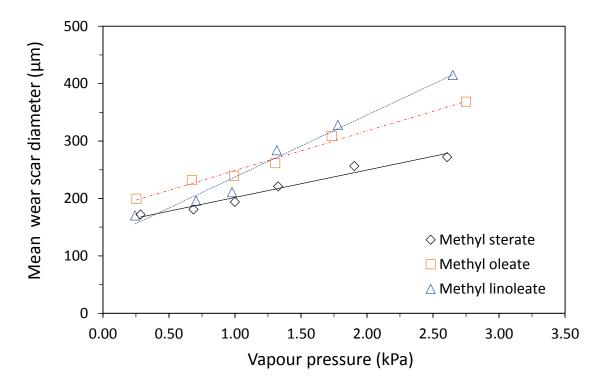


Figure 7 Effect of unsaturation of C18 FAMEs on MWSD.

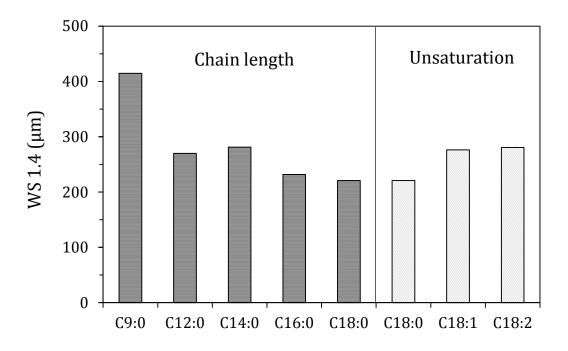


Figure 8 Normalized wear scar of FAMEs.

Fuel	Description	Molecular formula	Molecular weight (g/mol)	Viscosity at 40 °C (cSt)	Density at 15 °C (kg/m ³)a	Purity (% v/v)
Commercial fuels						
ULSD	Ultra-low sulphur diesel	$C_{14}H_{26.1}$	211.7	$2.70^{\rm a}$	827.1 ^a	
RME	Rapeseed methyl ester	$C_{19}H_{35.3}O_2$	294.4	4.53 ^a	883.7 ^a	
Oxygenated compounds						
Decanoic acid	Carboxyl (COOH)	CH ₃ (CH ₂) ₈ COOH	172.26	5.63 ^b	893 ^c	>98
Decanal	Aldehyde (CHO)	CH ₃ (CH ₂) ₈ CHO	156.27	1.72^{d}	830 ^c	>98
1-Decanol	Hydroxyl (OH)	CH ₃ (CH ₂) ₉ OH	158.28	8.04^{b}	829 ^c	>98
Methyl nonanoate	Esters (COOCH ₃)	CH ₃ (CH ₂) ₇ COOCH ₃	172.26	1.44 ^b	875 ^c	>97
Dipentyl ether	Ether (C-O-C)	$[CH_{3}(CH_{2})_{4}]_{2}O$	158.28	1.08^{b}	785 ^c	>98
2-Decanone	Ketone (C=O)	CH ₃ (CH ₂) ₇ COCH ₃	156.27	1.47 ^b	825 ^c	>98
Fatty acid methyl esters						
Methyl laurate	C12:0	$C_{13}H_{26}O_2$	214.34	2.43 ^b	873.28 ^e	>98
Methyl myristate	C14:0	$C_{15}H_{30}O_2$	242.40	3.30 ^b	868.18 ^e	>98
Methyl palmitate	C16:0	$C_{17}H_{34}O_2$	270.45	4.38 ^b	864.19 ^e	>97
Methyl stearate	C18:0	$C_{19}H_{38}O_2$	298.50	5.92 ^b	867.55 ^e	>96
Methyl oleate	C18:1	$C_{19}H_{36}O_2$	296.49	4.78^{b}	877.46 ^e	>99
Methyl linoleate	C18:2	$C_{19}H_{34}O_2$	294.47	4.25 ^b	893.18 ^e	>99

Table 1. Main properties of tested fuels, oxygenated compounds and fatty acid methyl esters.

^a [21]

^b [19]

^c [17]

^d [18]

^e [20]

Component Elements	С	Cr	Mn	Р	Si	S	Fe
Content (%)	0.98 - 1.10	1.30 - 1.60	0.25 - 0.45	≤ 0.025	0.15 - 0.30	\leq 0.025	balance

Table 2. Chemical composition of ANSI E-52100 [22].

Specimen	Hardness	Roughness
Ball	HRC 58-66	<0.05 🗆 m Ra
Disc	190-210HV30	<0.02 🗆 m Ra

Table 3. Hardness and roughness of specimens [23].

Salt	Temperature (°C)	Relative humidity (%)	Vapor pressure (kPa)
Sodium hydroxyde (NaOH)	24-27	7 –10	0.23 - 0.31
Potasium acetate (KCH ₃ CH ₂)	24-27	20 - 23	0.62 - 0.71
Magnesium chloride (MgCl ₂)	24-27	29 - 33	0.98 - 1.04
Potassium carbonate (K ₂ CO ₃)	24-27	40 - 43	1.28 - 1.40
Sodium bromide (NaBr)	24-27	54 - 58	1.73 – 1.90
Potassium chloride (KCl)	24-27	80 - 84	2.51 - 2.75

Table 4. Salts used for humidity control and ranges of humidity at laboratory temperature.

Fuel	Description	MWSD (µm) linear fit	HCF (µm/kPa)
ULSD	Ultra-low sulphur diesel	57.70 + 263.55	57.70
RME	Rapeseed methyl ester	85.80x + 145.27	85.80
Decaoic acid	Carboxyl (COOH)	22.92x + 74.674	22.92
Decanal	Aldehyde (CHO)	13.46x + 159.23	13.46
1-Decanol	Hydroxyl (OH)	14.98x + 360.27	14.98
Methyl nonanoate	Esters (COOCH ₃)	40.62x + 357.72	40.62
Dipentyl ether	Ether (C-O-C)	25.07x + 441.18	25.07
2-Decanone	Ketone (C=O)	99.80x + 496.14	99.80

Table 5. Proposed humidity correction factors for commercial fuels and oxygenated compounds.

Fuel	Description	MWSD (µm) linear fit	HCF (µm/kPa)
Methyl laurate	C12:0	45.83x + 205.65	45.83
Methyl myristate	C14:0	55.61x + 202.94	59.24
Methyl palmitate	C16:0	48.00x + 164.55	40.16
Methyl stearate	C18:0	47.75x + 153.95	47.75
Methyl oleate	C18:1	68.86x + 179.85	68.86
Methyl linoleate	C18:2	108.02x + 129.27	108.02

Table 6. Proposed humidity correction factors for individual fatty acid methyl esters.