Effect of fatty acid composition of methyl and ethyl esters on the lubricity at different humidities

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ABSTRACT

Lubricity of individual fatty acid methyl or ethyl esters and biodiesel fuels has been measured using a high frequency reciprocating rig (HFRR). Tests have been carried out varying the ambient humidity to assess the effect of this parameter on the lubricity of the fuels. The European standard proposes a single humidity correction factor for all the fuels, regardless their composition. It has been proved in this study that this factor is not constant and it depends on the fuel composition. For this reason two different correlations have been proposed for the estimation of the humidity correction factor and normalized wear scar as a function of different fuel compositional characteristics. The influence of the water content on the lubricity and the relationship between humidity and water content of the fuel has been studied revealing that the effect of the air humidity is an indirect effect of the hygroscopy of the fuel.

1. Introduction

The improvement of common-rail systems in diesel engines has allowed the transport companies to develop new strategies to increase engine efficiency and reduce pollutant emissions. One of the strategies developed by the manufacturers is to use higher injection pressures to atomize the fuel, leading to better air mixing, faster evaporation and more efficient combustion process. Severely-loaded systems such as injectors or pressure pumps need fuels with high lubricating capacity to avoid any wear problem. However, almost all of the petroleum-based diesel fuels available in Europe and North America are now of ultra-low sulfur diesel (ULSD) type, to accomplish with the new environmental policies about limiting sulfur. The low sulfur diesel fuel has poor lubricity, caused by the removal of polar oxygen and nitrogen compounds,

which happens during the process of sulfur species extraction. These polar compounds are adsorbed on the rubbed metal surfaces providing a protective layer that reduces adhesion and limit friction or wear [1].

To restore the lubricity of these fuels, the use of additives or blends with another fuel of enhanced lubricity is required [2]. For this reason the influence of different compounds on the lubricity of diesel fuels has been tested and oxygenated compounds were ordered regarding their lubricity enhancing potential (COOH > CHO > OH > COOCH$_3$ > C=O > C—O—C) [3]. Biodiesel, an alternative diesel fuel derived from the transesterification of vegetable oils or animal fats, can be used in blends with diesel to improve the lubricity, because biodiesel contains polar oxygenated compounds. Moreover, biodiesel is an environment-friendly option that can be cheaper than other kind of additives. Biodiesel-diesel blends have been widely studied and it is well known that biodiesel reduces the particulate matter and CO emissions and increases cetane number and flash point of diesel in blends [4–6]. In

addition, biodiesel may not require engine modifications when used in blends up to 20% (m/m) in diesel, as far as cold-flow properties are the required ones for the climate conditions [7]. Biodiesel can be produced with methanol or ethanol resulting in fatty acid methyl esters (FAMEs) or ethyl esters (FAEEs), respectively, both compounds having inherent good lubricity. Generally there are fewer studies of FAEEs because the lower price of methanol has made FAMEs to be widely used and also because the base catalyzed production of FAEEs is more difficult than the production of FAMEs. During the course of reaction, emulsions are usually formed, which in the case of methanolysis easily break down but, in ethanolysis are more stable, probably because of the formation of monoglycerides [8], and complicate the separation and purification of esters. Nevertheless, FAEEs have been industrially produced in places like Brazil and the development of new biotechnologies for the production of bioethanol can favor the use of ethanol, what would convert the biodiesel in a total renewable source of energy [9]. The amounts of biodiesel needed to improve the lubricity of the diesel fuel are low. In fact, previous studies show how the reduction of lubricity tends to stabilize at concentrations higher than 1% by volume [10]. It is also interesting the effect on lubricity of the impurities of biodiesel, as free fatty acids or monoacylglycerols. Both compounds, although present in minimum amounts (≈ 100 ppm), are major contributing factors to improve the lubricity of blends of biodiesel with diesel [11].

Lubricity is commonly measured through the high frequency reciprocating rig (HFRR) test due to the ability of providing a wide range of wear mechanisms [12]. It has been proved recently that the HFRR is also suitable for evaluating the wear performance of fuels in more severe contact conditions than those that may exist in future fuel injection equipment [13]. The test methods are specified in standards EN ISO 12156-1:2006 [14] and ASTM D 6079 [15] for Europe and US, respectively. In the US the ASTM D975 [16] limit is 520 μm, in Europe the EN 590 [17] limit is 460 μm, while the World Wide Fuel Charter recommends a maximum wear scar of 400 μm for diesel fuels to be commercialized in markets with advanced or highly advanced requirements for emission control and fuel efficiency [18].

Previous studies have shown that the lubricating properties of the fuel, hence the size of the wear scar in the HFRR test, are influenced by the relative humidity in the air, especially when low load is applied and oxidative wear is predominant [19]. Because of this, the ISO standard proposes a correction of the measured wear scar depending on the vapor pressure, using the so-called humidity correction factor (HCF) which is set to 60 μm/kPa for all the fuels, regardless of their composition. This unchanged factor has been proved to underestimate or overestimate lubricity when dealing with different kind of fuels [20] and depends on the fuel chemical composition.

This work continues a previous study on lubricity [20], in this case focusing on biodiesel fuels and components. HCFs and wear scars of FAMEs and FAEEs are measured to study the influence of the biodiesel composition on the lubricity, taking into account the water content in the fuel and the effect of hygroscopy on the change of lubricity at different ambient humidities.

2. Fuels and experimental schedule

The following fuels were tested with the HFRR at the laboratory of the Fuels and Engines Group of the University of Castilla-La Mancha (UCLM):

- Pure methyl esters: Methyl laurate, myristate and stearate were donated by the University of Birmingham (these compounds were purchased from Sigma-Aldrich). Methyl palmitate was purchased from Alfa Aesar. The main characteristics of pure methyl esters are shown in Table 1.
- Synthetic ethyl esters were manufactured from pure fatty acids at the Universidad Politécnica de Madrid (UPM). Fatty acids were purchased from Sigma Aldrich and were transformed into the fatty acid ethyl esters through an esterification process described in the literature [21]. The purity of the esters was tested following the EN 14103 method. A Hewlett-Packard 5890 series II gas chromatograph equipped with FID detector and split/splitless injector and an HP-Wax column (30 m × 0.32 mm i.d. × 0.15 μm) of polyethylene glycol was used for the analysis. Properties of these compounds are shown in Table 1 and results of the chromatographic analysis are shown in Table 2.
- Biodiesel fuel (FAME) from palm oil produced and donated by Antioquia University, and fulfils EN 14214. The fatty acid profile was analysed with gas chromatography as previously described and the results are provided in Table 3.
- Biodiesel fuels (FAEEs) from different kind of oils were also produced at UPM following a transesterification method described in the literature [22]. The composition was tested through gas chromatography and the results are shown in Table 4.

Table 1
Main properties of the methyl and ethyl esters.

Fuel	Molecular formula	Carbon number in the acid chain	Average number of double bonds	Molecular weight (g/mol)	Melting point (°C)[a]	Viscosity at 40 °C (mPa·s)[b]	Density at 15 °C (kg/m³)[c]
Methyl							
Methyl laurate	$C_{13}H_{26}O_2$	12	0	214.11	4–5	2.08	873.28
Methyl myristate	$C_{15}H_{30}O_2$	14	0	242.13	18	2.84	868.18
Methyl palmitate	$C_{17}H_{34}O_2$	16	0	270.15	32–35	3.76	864.19
Methyl stearate	$C_{19}H_{38}O_2$	18	0	298.17	37–41	4.99	867.55
Ethyl							
Ethyl caproate	$C_8H_{16}O_2$	6	0	144.06	−67[d]	–	878.56
Ethyl caprate	$C_{12}H_{24}O_2$	10	0	200.1	−20[d]	1.60	873.34
Ethyl laurate	$C_{14}H_{28}O_2$	12	0	228.12	−2[e]	2.22	867.96
Ethyl myristate	$C_{16}H_{32}O_2$	14	0	256.14	11–12[a]	2.99	867.65
Ethyl palmitate	$C_{18}H_{36}O_2$	16	0	284.16	24–26[a]	3.96	864.39
Ethyl stearate	$C_{20}H_{40}O_2$	18	0	312.18	34–38[a]	5.03	858.72
Ethyl oleate	$C_{20}H_{38}O_2$	18	1	310.18	−32[a]	4.21	877.18
Ethyl linoleate	$C_{20}H_{36}O_2$	18	2	308.18	–	–	883.18

[a] [23].
[b] [24].
[c] [25].
[d] [26].
[e] [27].

Table 2
Composition of the synthetic ethyl esters.

FAEE, wt%	Ethyl caproate	Ethyl caprate	Ethyl laurate	Ethyl myristate	Ethyl palmitate	Ethyl stearate	Ethyl oleate	Ethyl linoleate
Ethyl caproate	96.08							
Ethyl caprate		97.88						
Ethyl laurate	3.92		92.28					
Ethyl myristate				100			2.07	
Ethyl palmitate		2.12			100	2.05	5.38	
Ethyl palmitoleate							6.54	
Ethyl stearate						97.75		
Ethyl oleate			7.72				76.41	
Ethyl linoleate							8.80	100
n[a]	8.15	12.09	14.35	16	18	19.96	19.61	20
db[b]	0	0	0.08	0	0	0	1.06	2

[a] Weighted-average number of carbon atoms in the FAEE.
[b] Weighted-average number of double bonds in the FAEE.

Table 3
Fatty acid profile of the palm-oil biodiesel fuel.

FAME, wt%	Palm
Methyl laurate	0.22
Methyl myristate	0.83
Methyl palmitate	42.52
Methyl palmitoleate	0.13
Methyl stearate	4.77
Methyl oleate	41.27
Methyl linoleate	10.09
Methyl linolenate	0.16
Ester content	100
n[a]	18.05
db[b]	0.62

[a] Weighted-average number of carbon atoms in the FAME.
[b] Weighted-average number of double bonds in the FAME.

Table 5
Salts used to reach different vapor pressure in the HFRR chamber.

Salt	Temperature (°C)	Relative humidity (%)	Vapor pressure (kPa)
Sodium hydroxide (NaOH)	25–28	8–9	0.25–0.35
Potassium acetate (KCH₃CH₂)	25–28	21–22	0.66–0.86
Magnesium chloride (MgCl₂)	25–28	32–33	1.01–1.29
Potassium carbonate (K₂CO₃)	25–28	42–43	1.33–1.68
Sodium bromide (NaBr)	25–28	55–56	1.74–2.10
Potassium chloride (KCl)	25–28	82–83	2.60–3.20

Every methyl or ethyl ester fuel was tested for a minimum of two humidities (or vapor pressures), using for that the equilibrium of the salts described in Table 5. The salts were purchased in Panreac and are of synthesis grade.

3. Experimental equipment and procedure

Lubricity was measured with a HFRR (PCS Instruments, London, U.K.) following the European EN ISO 12156-1:2006 standard and the ASTM D 6079 standard. The volume of the fuel samples was 2 mL and its temperature was set to 60 °C. A steel ball and a steel disk were completely submerged in the test fuel and put in contact with each other. The steel ball is held with a vibrator arm and loaded with 200 g mass. Then a vibration of 1 mm at a frequency of 50 Hz for 75 min causes a wear scar on both the ball and the disk. The wear scar on the ball, that represents the lubricating efficiency, was estimated by measuring the mean diameter of the scar (MWSD) obtained from the length of the wear scar in the axis parallel and perpendicular to the ball displacement using a stereomicroscope Optika SZR1 equipped with 100× magnification lens.

All tests were made inside a climatic chamber where the ambient temperature and humidity were controlled with the use of salts. The climatic chamber is a specific cabinet produced by PCS instruments. Temperature and relative humidity are controlled and instantaneously displayed on the HFRR board.

Prior to use, the test components were submerged into 10 min ultrasonic-baths, first two using toluene and a final cleaning bath with acetone. Experiments were repeated twice and repeatability was demonstrated to be less than 20 μm [28], which is acceptable according to the European standard which has shown a repeatability of 63 μm and to the American standard that has a repeatability of 80 μm (slightly higher because of the non-existent correction for the ambient humidity).

Water content in the fuel samples was measured with a Karl Fischer 756 KF Coulometer from Metrohm, following the method described in standard EN-12937.

Table 4
Composition of the biodiesel fuels made of ethyl esters from different sources of oil.

FAEE, wt%	Waste frying oil	Soybean	Sesame	Linseed	Camelina	Rapeseed
Ethyl myristate	0.44	0	0	0.95	0	0
Ethyl palmitate	14.17	12.81	9.54	6.9	6.9	5.04
Ethyl palmitoleate	2.37	0	0	0	0	0
Ethyl stearate	3.93	6.52	5.88	4.46	2.88	9.22
Ethyl oleate	66.4	29.37	40.27	21.34	17.37	59.55
Ethyl linoleate	10.33	46.06	43.13	17.27	33.47	17.74
Ethyl linolenate	0.77	4.92	0.34	49.08	26.03	6.59
Ethyl arachirate	0	0.32	0	0	1.33	0.51
Ethyl gadoleate	1.59	0	0.84	0	12.01	1.36
Ester content	97.68	98.72	97.58	99.27	96.79	98.78
n[a]	19.65	19.73	19.81	19.81	20.09	19.92
db[b]	0.93	1.36	1.28	2.03	1.74	1.16

[a] Weighted-average number of carbon atoms in the FAEE.
[b] Weighted-average number of double bonds in the FAEE.

4. Water correction factors

The standard UNE-EN ISO 12156-1 proposes the following equation to calculate the wear scar of the samples, with a correction depending on the temperature and relative humidity of the air measured through the vapor pressure:

$$WS1.4 = MWSD + HCF(1.4 - \overline{p_v}) \tag{1}$$

where $WS1.4$ is the wear scar normalized to a vapor pressure of 1.4 kPa and $\overline{p_v}$ is the mean vapor pressure during the test time. HCF is, according to the standard, a constant value of 60 μm/kPa, but a value depending on the composition of each fuel would predict more accurately the lubricating efficiency. This factor was obtained by differentiating Eq. (1) with respect to the vapor pressure and solving the equation for HCF:

$$HCF = \frac{dMWSD}{d\overline{p_v}} \tag{2}$$

The hygroscopy of a fuel depends on its composition and accounts for the amount of water which is absorbed from humid air (quantified with its humidity or vapor pressure). In a previous study [20] the effect of humidity on the wear scar was proposed to be an indirect effect of the hygroscopy of the fuel. Therefore, since each fuel has a different hygroscopy, depending on its composition, a constant value of 60 μm/kPa would not be accurate to correct the effect of vapor pressure for all the fuels. The new parameters proposed to measure this effect are derived from the psychrometry theory:

– The water–air correction factor (WACF):

$$WACF = \frac{dMWSD}{dY_{H_2O/air}} = HCF\frac{dp_v}{dY_{H_2O/air}} \tag{3}$$

– The water-fuel correction factor (WFCF):

$$WFCF = \frac{dMWSD}{dY_{H_2O/fuel}} \tag{4}$$

– The hygroscopy (Hy) of the fuel:

$$Hy = \frac{dY_{H_2O/fuel}}{dY_{H_2O/air}} = \frac{\frac{dMWSD}{WFCF}}{\frac{dMWSD}{WACF}} = \frac{WACF}{WFCF} \tag{5}$$

where $Y_{H_2O/air}$ and $Y_{H_2O/fuel}$ are the mass fraction of water vapor in the humid air and the mass fraction of water in the fuel respectively.

5. Results and discussion

5.1. Lubricity of FAMEs and FAEEs

5.1.1. Humidity correction factor (HCF)

The change in the non-corrected wear scar through different vapor pressures between 0.25 and 2.75 kPa can be observed in Figs. 1 and 2. The relation between the MWSD and the vapor pressure is approximately linear and Eq. (2) can be applied to calculate the different HCF. The linear equations which best fitted the experimental results with the correction factors for all the methyl and ethyl esters are collected in Tables 6 and 7. The R-squared value of the lines is always higher than 0.9 which proves a good linear correlation between the data. As can be seen in Fig. 2 only a few lubricity tests could be performed at different humidities for the different fuels because not enough quantity was available for these fuels. Therefore the accuracy in the HCF calculation could be affected.

No clear correlation was found between number of carbons and the value of HCF as it can be seen in Fig. 3 but the HCFs of FAMEs
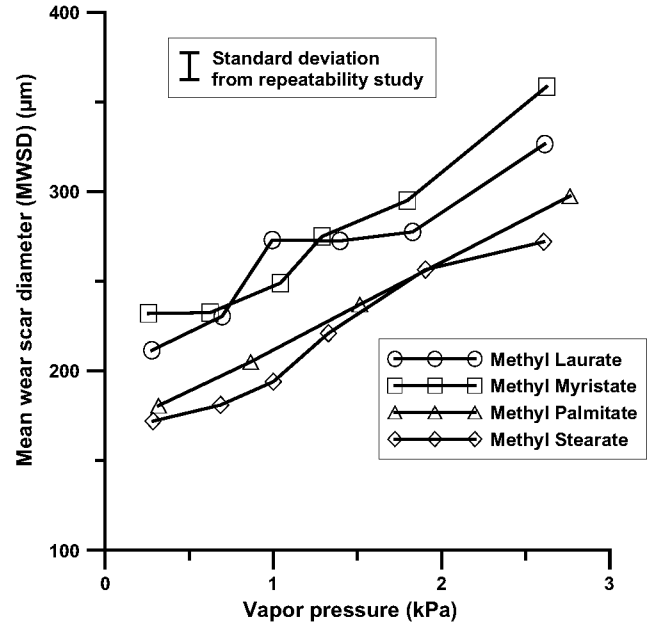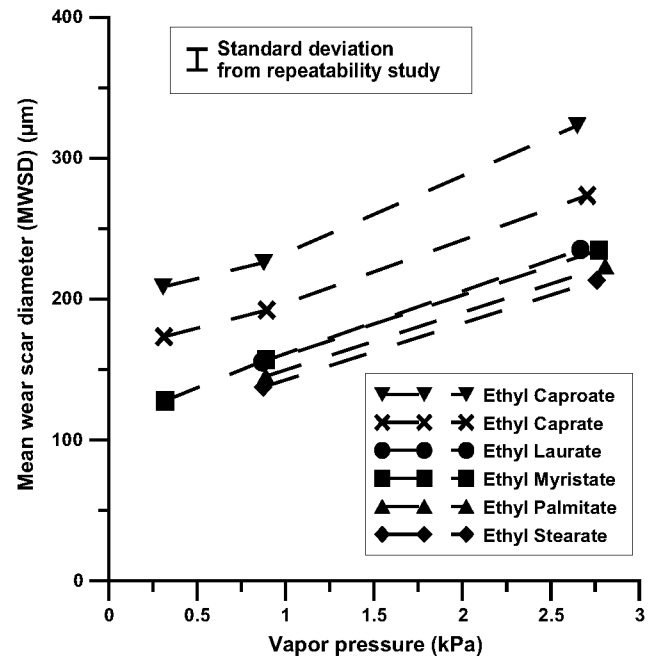

Fig. 1. MWSD of FAMEs.

Fig. 2. MWSD of FAEEs.

Table 6
HCFs of FAMEs.

FAMEs	MWSD (μm) linear fit	HCF (μm/kPa)	R^2
Methyl laurate	$45.83p_v + 205.65$	45.83	0.9108
Methyl myristate	$55.61p_v + 202.94$	55.61	0.9538
Methyl palmitate	$48.00p_v + 164.55$	48.00	0.9997
Methyl stearate	$47.75p_v + 153.95$	47.75	0.9643

are always higher than those of FAEEs, for the same length of the carbon chain. In the case of FAEEs, generally an increase in the number of carbons of the fatty acid chain leads to a reduction in the HCF. Comparing the values of HCF obtained with the standard

Table 7
HCFs of FAEEs.

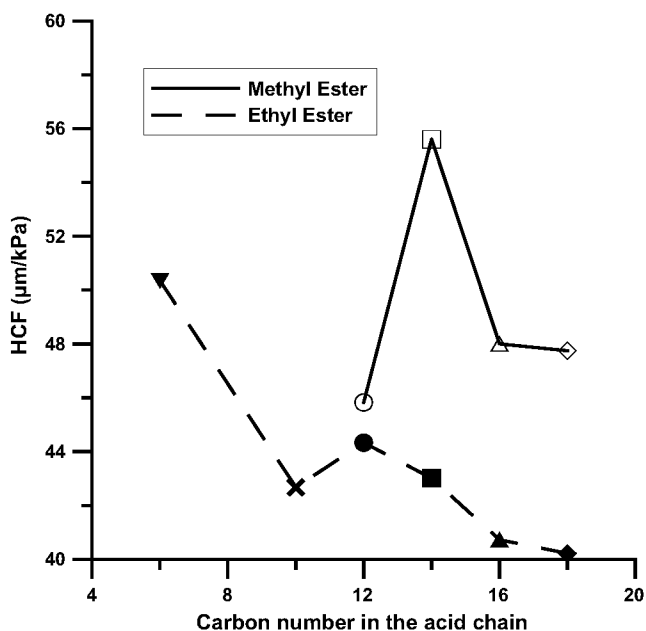| FAEEs	MWSD (μm) linear fit	HCF (μm/kPa)	R^2
Ethyl caproate	$50.35p_v + 188.20$	50.35	0.9911
Ethyl caprate	$42.67p_v + 157.30$	42.67	0.9968
Ethyl laurate	$44.33p_v + 116.92$	44.33	–
Ethyl myristate	$43.01p_v + 116.02$	43.01	0.9982
Ethyl palmitate	$40.72p_v + 108.94$	40.72	–
Ethyl stearate	$40.22p_v + 102.30$	40.22	–

Fig. 3. Variation of HCF with the number of carbons.

value of 60 μm/kPa given by the EN 12156-1, all of them are below the standard. Therefore the use of HCF set by EN-12156-1 for the calculation of the corrected lubricity (WS1.4) would be wrong, overestimating or underestimating the wear scar produced by the fuels, depending on the vapor pressure when the lubricity test is carried out [20].

5.1.2. Influence of composition on lubricity

The lubricity results (WS1.4) for pure FAMEs and synthetic FAEEs are reported in Figs. 4 and 5. To obtain these results the HCF values calculated in the previous section have been used. Fig. 4 shows a clear decreasing trend of the wear scar with the increase of the number of carbons in the fatty acid chain. This effect agrees with previous studies where it is shown that molecules with the same structure and functional group, improve their lubricity with the increase in their molecular weight [3]. Especially in the case of FAEEs, a more sudden decrease of wear scar is observed between the caprylate and laurate ethyl ester while for shorter and longer carbon chain the wear scar seems to stabilize. Also, it can be noticed in Fig. 4 that both methyl and ethyl esters remain below the maximum wear scar value that sets the EN 590 Standard.

Results show that FAEEs have better lubricity than FAMEs, probably because of their different molecular conformation. Short alkyl esters possess polarity in their head-groups that provide an amphipathic nature resulting in a head-to-head alignment of molecules [29]. To the contrary, larger alkyl esters have non-polar head-groups that are able to neutralize the forces between more polar portions of the head-group aligning themselves in a head-to-tail arrangement with much larger molecular spacing.
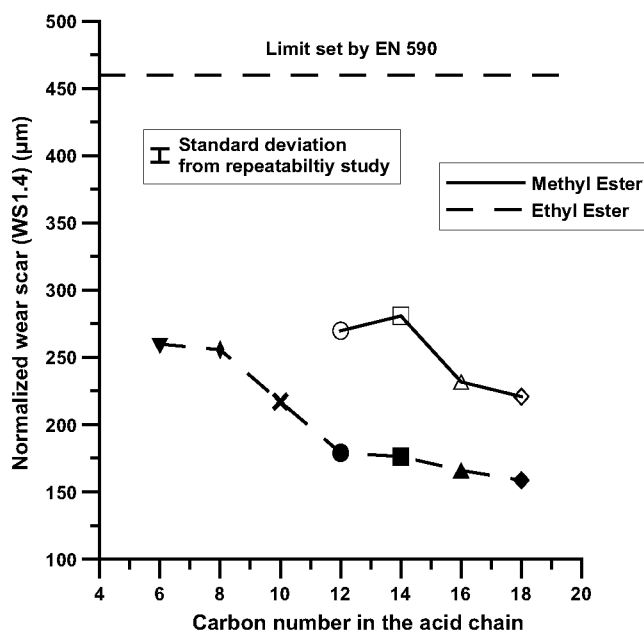

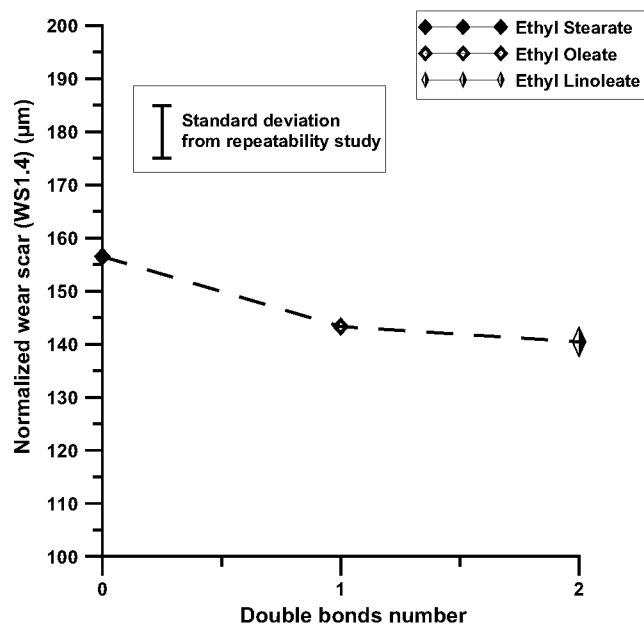**Fig. 4.** Normalized wear scar of FAMEs and FAEEs.

Fig. 5. Effect of the unsaturation of C_{18} FAEEs on the lubricity.

Such voluminous head-groups disrupt the spacing between individual molecules in the crystal structure causing rotational disorder in the hydrocarbon tail-group. In the case of FAEEs, the length of the alcohol chain is still short enough to let the molecules organize in a head-to-head arrangement, producing better lubricity due to the length increase of the complete structure.

Fig. 5 shows that the increase in the unsaturation causes slightly better lubricity, in accordance with previous studies [30]. It is important to indicate that this effect is opposite to the behavior of these compounds concerning their viscosity. The viscosity decreases with the number of double bonds, so between the three compounds depicted in the graphic, ethyl linoleate is the one with better lubricity but worse viscosity, confirming that viscosity and lubricity not always are correlated, especially in low-sulfur fuels [1].

5.2. Lubricity of biodiesel fuels

5.2.1. Humidity correction factor (HCF)

Fig. 6 shows the relationship between *MWSD* and vapor pressure for different biodiesel fuels from different oils. As can be seen in Fig. 6, only four lubricity tests were carried out at different humidities for the different fuels because not enough quantity was available for these fuels. Therefore the accuracy in the *HCF* calculation could be affected. An approximately linear relation was found between the vapor pressure and the *MWSD* (the R-squared of all the estimation lines is near 1). The slope of the lines can be calculated using Eq. (2) to estimate the *HCFs* of the fuels. The best-fit equations together with the correction factors for the biodiesel fuels are collected in Table 8. It is important to emphasize that *HCF* values are very similar for all the fuels tested and oscillate between 38 and 46 μm/kPa. This range is similar to that observed for pure methyl and ethyl esters with carbon number higher than 14 (shortest ester composing the biodiesel fuels tested) in Section 5.1.1.

As previously noted for the individual FAMEs or FAEEs, all the fuels have an *HCF* lower than 60 μm/kPa. Therefore, the use of the standard would overestimate or underestimate the wear scar produced, and individual values of *HCF* for each type of fuel would improve the precision in the estimation of the WS1.4.
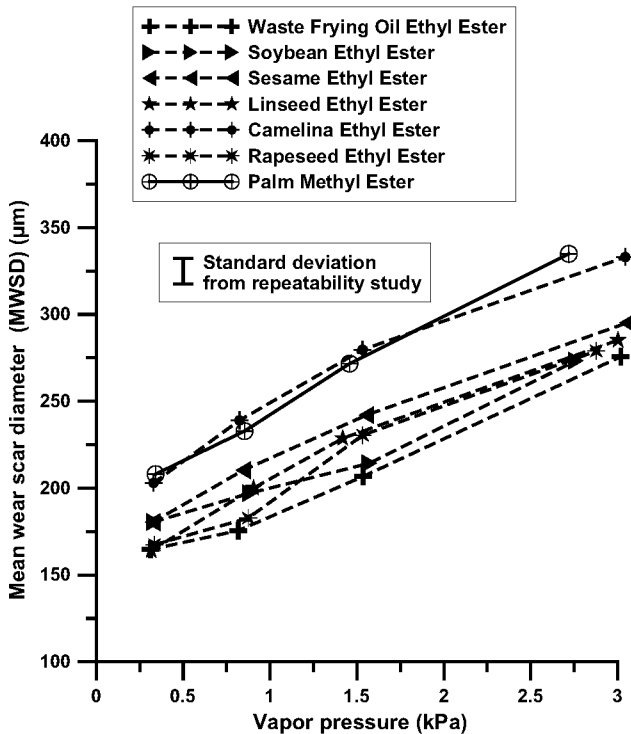

Fig. 6. *MWSD* of biodiesel fuels.

5.2.2. Influence of composition on lubricity

The lubricity results of biodiesel fuels are reported in Table 9. To obtain these results the *HCF* values calculated in the previous section have been used. The table shows that all the biodiesel fuels accomplish the American (with normalized wear scars below 520 μm) and European (below 460 μm) standards. As can be observed in Table 4, the biodiesel fuels tested have different average number of carbon atoms and different average number of double bonds. These factors, together with the eventual impurities, are expected to have some influence on the lubricity of the fuels, as reported in other studies [3,30]. Normalized wear scars are in general slightly higher than the values previously shown in Figs. 4 and 5 for pure ethyl esters with more than 14 carbon atoms and different degrees of unsaturation. In any case, among the tested biodiesel fuels, the normalized wear scars obtained are very similar and not differing in more than 60 μm, approximately, which is close to the minimum difference between tests to be considered significant in EN ISO 12156-1.

5.3. Correlation for WS1.4 and HCF for methyl and ethyl esters

As commented above, the biodiesel fuels tested have different average number of carbon atoms and different average number of double bonds and these factors are expected to have some influence on the lubricity of the fuels and on the effect of humidity. Therefore, two different correlations have been proposed to calculate the normalized wear scar (*WS1.4*) and the humidity correction factor (*HCF*) as a function of the carbon atoms number, the degree of unsaturation (that can be measured by the average number of double bonds) and the type of transesterification. To obtain these correlations all the results presented previously with pure methyl and ethyl esters and biodiesel fuels have been used. The following equations have been obtained to estimate the *WS1.4* (Eq. (6)) and the *HCF* (Eq. (7)) using these three parameters.

$$WS1.4 = 381.54 - 8.17n + 49.05db - 66.79(m - 1) \quad R^2 = 0.845 \tag{6}$$

$$HCF = 60.65 - 0.65n + 2.33db - 7.77(m - 1) \quad R^2 = 0.619 \tag{7}$$

where
    n: Average number of carbon atoms.
    db: Average number of double bonds.
    m: Number of carbon atoms of the alcohol used for transesterification (1 if the transesterification was carried out with methanol and 2 if the transesterification was carried out with ethanol).

As can be observed in Eq. (6), as the average number of carbon atoms (*n*) increases, the normalized wear scar (*WS1.4*) decreases. In previous studies, fuels were shown to improve their lubricity as their molecular weight was increased [3]. Therefore, the results obtained with Eq. (6) are in agreement with those previous studies.

Table 8
HCF of biodiesel fuels.

	Fuel	*MWSD* (μm) linear fit	*HCF* (μm/kPa)	R^2
FAME	Palm	$53.87p_v + 189.52$	53.87	0.9976
FAEEs	Waste frying oil	$42.23p_v + 145.68$	42.23	0.9898
	Soybean	$38.16p_v + 163.45$	38.16	0.9749
	Sesame	$41.17p_v + 172.48$	41.17	0.9891
	Linseed	$43.94p_v + 157.50$	43.94	0.9800
	Camelina	$46.58p_v + 196.95$	46.58	0.9721
	Rapeseed	$45.44p_v + 151.05$	45.44	0.9799

Table 9
Normalized wear scar of biodiesel fuels.

	Fuel	*WS1.4* (μm)
FAME	Palm	264.93
FAEE's	Waste frying oil	204.79
	Soybean	216.87
	Sesame	230.12
	Linseed	219.02
	Camelina	262.16
	Rapeseed	214.67

Regarding the type of transesterification, it can be seen in Eq. (6) that transesterification with ethanol, instead of methanol, has an enhanced effect in lubricity. This result is also in agreement with the results obtained in Fig. 4. The correlation for *HCF* (Eq. (7)) has not such a good R-squared coefficient. The reason for this could be that the number of lubricity tests carried out at different humidities is not enough and this has a negative impact in the accuracy of the estimated *HCF*. As can be observed in Eq. (7), as the average number of carbon atoms increases and the average number of double bonds decreases, the *HCF* obtained becomes smaller than the *HCF* set by EN ISO 12156-1. Therefore the Standard overestimates the *HCF*. Furthermore, transesterification with ethanol contributes to decrease the humidity correction factor for every biodiesel fuel. The effect of the type of transesterification is more significant in the *HCF* than the effect of the carbon atoms number and the double bonds number. The results obtained with the two correlations are shown in Figs. 7 and 8.

5.4. Influence of the water content in the fuel on the lubricity

In previous sections, the effect of humidity in the ambient air on the fuel lubricity was presented. In this section the effect of fuel water content in the fuel on its lubricity is analysed by addition of water to the fuels tested. Four pure methyl esters and a biodiesel fuel were selected to characterize the effect of the water content on the lubricity of the fuel. They were all tested under potassium
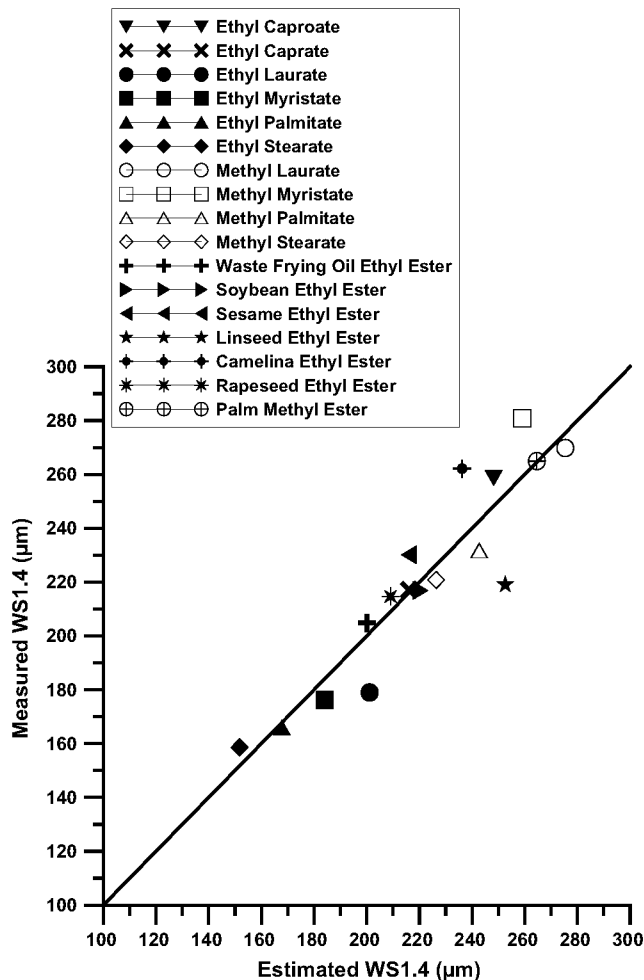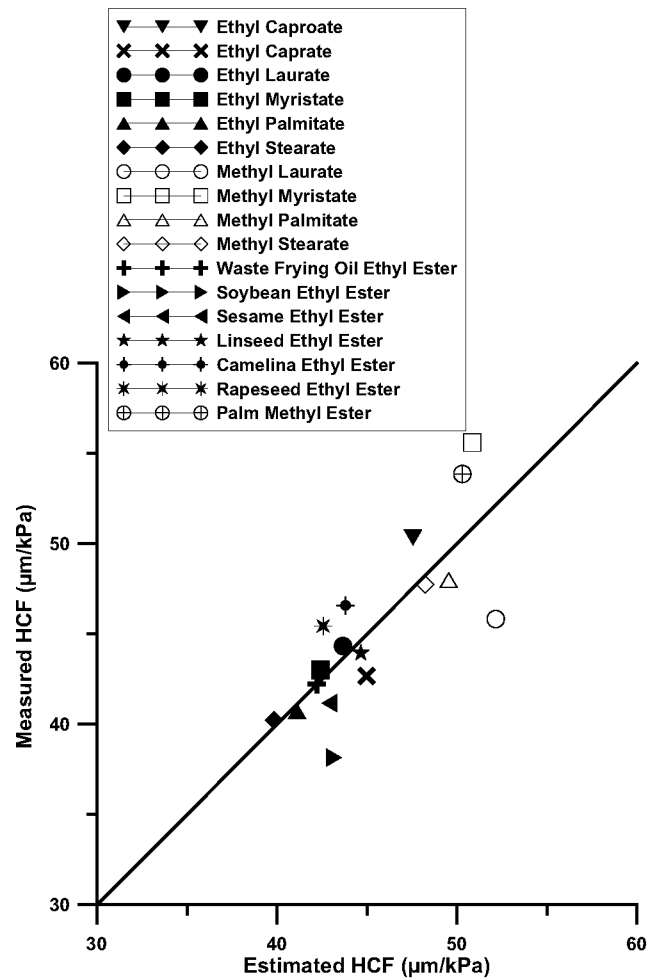
Fig. 8. Correlation for the estimation of *HCF* and the experimental values.

acetate environment (vapor pressure from 0.66 to 0.86 kPa) and laboratory ambient pressure of 94.25 kPa. Fig. 9 shows that two water additions were made to each fuel, of approximately 100 and 200 ppm. In all samples, an increase in water content produces an increase in wear scar. The presence of water prevents the formation of the third body debris layer on the metal surface [31] and thus adhesive wear is not likely to occur to the same extent. According to [32], this third body layer is often composed of particles detached from the rubbing surfaces which separate the surfaces in contact, avoiding direct interactions. For this reason water content present in the fuel cause a major abrasion and corrosion.

WACF can be obtained using the developed formula of Eq. (3) [20] and *WFCF* can be estimated using Eq. (4). Results are reported in Fig. 10. Dots connected with solid lines represent saturated methyl esters, and isolated dot corresponds to the biodiesel fuel tested (with some degree of unsaturation). It can be observed that the tendency is the same for *WACF* and for *WFCF*. For the same type of chemical compound (in this case methyl esters), when the *WACF* increases, the same does the *WFCF* and vice versa. Therefore, water present in environment or water contained in the fuel affect in the same way to the fuel lubricity. This is consistent with the direct effect of the fuel composition on both the normalized wear scar and the humidity correction factor, as shown in Eq. (7), and it also proves that the water content in the fuels is the main cause of the increase in the wear scar when humidity increases (Fig. 11) [20]. The main implication of this conclusion is that the well-known
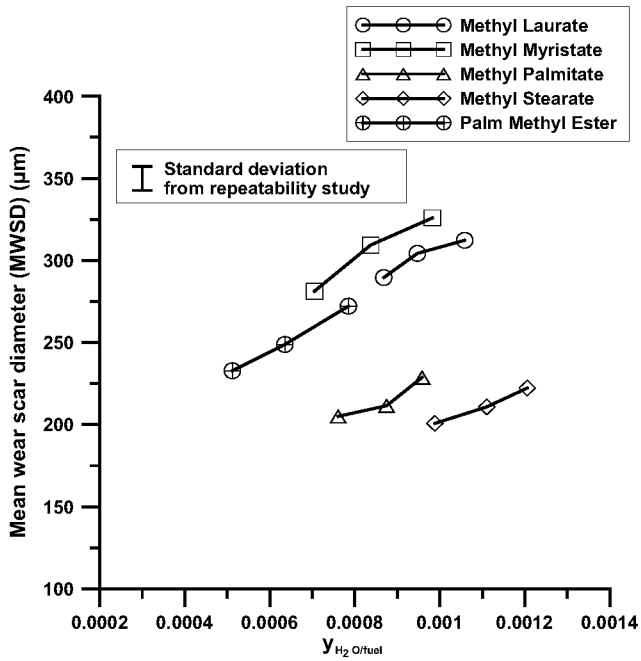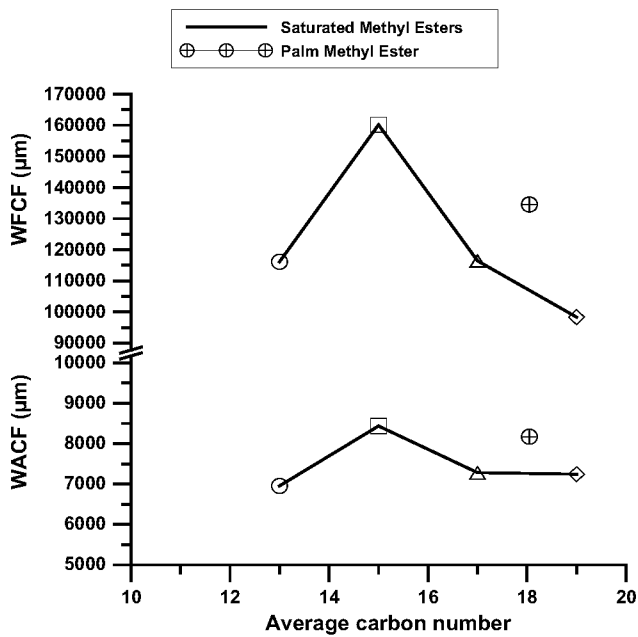
Fig. 7. Correlation for the estimation of *WS1.4* and the experimental values.

Fig. 9. Influence of water content in the MWSD.

Fig. 10. *WACF* and *WFCF* of pure methyl saturated esters and biodiesel fuel.

Fig. 11. Effect of water on lubricity.

Fig. 12. Hygroscopy of pure saturated methyl esters and biodiesel fuel.

6. Conclusions

A high frequency reciprocating rig (HFRR) has been used to study the influence of composition and ambient humidity of the individual components of biodiesel (methyl and ethyl esters) and also of actual biodiesel fuels from different oils on their lubricity. A correlation has been proposed to calculate the normalized wear scar of a biodiesel fuel as a function of the average number of carbons of the acid chain, the average number of double bonds (as a measure of the unsaturation) and the alcohol used for transesterification. The influence of humidity on the lubricity of methyl and ethyl esters and biodiesel fuels has also been studied through the humidity correction factor (*HCF*). This factor is approximated by the lubricity standard to 60 μm/kPa and all the measurements obtained in this work are below this value. Consequently, the lubricity of biodiesel fuels is underestimated or overestimated (depending on the ambient vapor pressure) when the factor provided by the standard is used. An additional correlation has been proposed to calculate this factor. From both correlations, it can be concluded that when the number of carbon atoms in the acid chain or in the alcohol used for transesterification increase, both

benefits in lubricity of biodiesel fuels could be counteracted by their high hygroscopy, which tends to capture water from the ambient air and thus reduce their lubricating properties, as far as they are largely exposed to open atmospheres.

Using the two mentioned parameters, the hygroscopy of each ester can be calculated using Eq. (5) (Fig. 12). In this case, the effect of the carbon number on the hygroscopy is minor, and variations are mainly attributed to inaccuracies in the determination of the effects of water in both: the fuel (*WFCF*) and the ambient air (*WACF*). Also, some effect of unsaturation to decrease hygroscopy can be appreciated. However, differences are small and the amount of data is not enough to guarantee the significance of this trend.
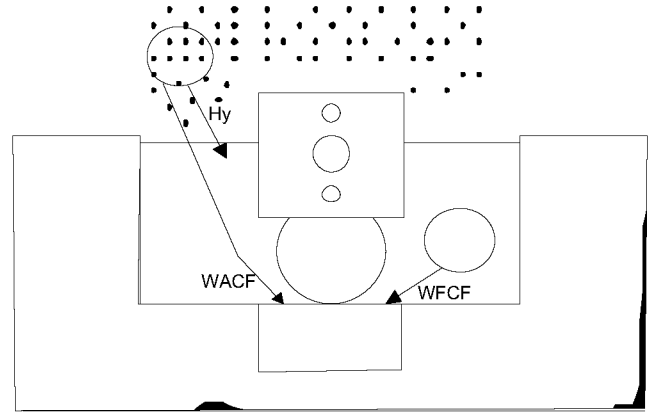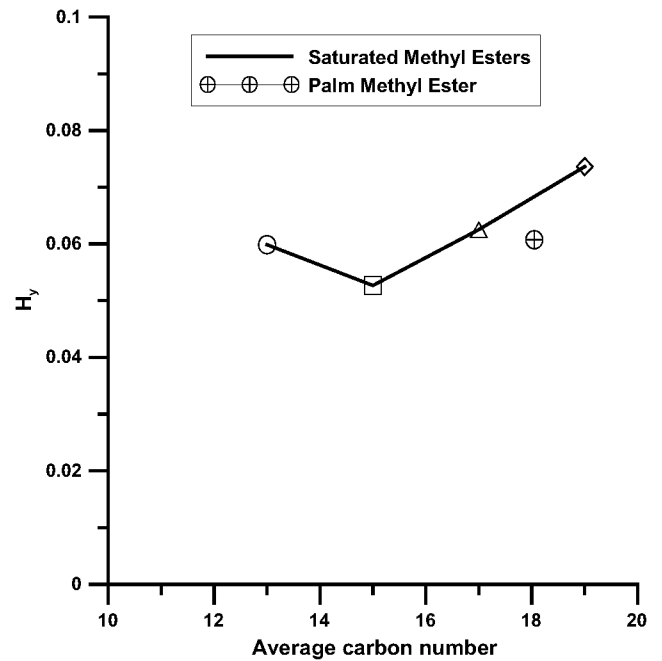
the normalized wear scar and the humidity correction factor decrease. The effect of the unsaturation on the wear scar is not so clear because it was opposite for pure esters than for biodiesel fuels. These correlations are useful to predict the lubricity of a biodiesel fuel, as well as the effect of humidity on the lubricity, from its fatty acid profile, with good accuracy, as far as the content of impurities in the biodiesel is small enough. Finally, it has been proved that the change in lubricity at different humidities (HCF) is derived from the different chemical composition of the fuel, and also that it is the water content in the fuel what mainly leads to an increase in the wear scar. This implies that the benefits in lubricity of biodiesel fuels could be counteracted by their high hygroscopy when they are exposed to open air for long time.

Acknowledgments

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