

Research Article

Tribological Performance of Si-Doped Hydrogenated Diamond-Like Carbon Coatings in Different Biodiesel

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In this paper, two kinds of different biodiesel were tested in terms of their impact on wear resistance of Si-DLC coated 100Cr6 flat worn by an oscillating 100Cr6 ball. The knowledge about the tribological behaviour of different types of biodiesel is rare. Rape and soybean are two of the most common natural sources for biodiesel production. Also, if the quality of biodiesel seems to be similar and, according to the demands, biodiesel from different natural origin could affect changes in the tribological behaviour. Although, soybean methyl ester (SME) gives the best results at room temperature wear tests, 150°C SME reaches wear rates of Si-DLC flat against 100Cr6 ball almost double as high as rapeseed methyl ester (RME). It is evident that, with increasing fraction of oxidation stabilizer $C_{23}H_{32}O_2$, the wear rate increases. For silicon doped hydrogenated diamond-like carbon is especially suitable, for use in biodiesels, where certain fraction of humidity, dissociated water, or polar functional groups may present.

1. Introduction

Biomass and biodiesel are used in a strongly increasing amount for automotive applications, power generation, or energy for buildings and housings. There is an increasing necessity for environment-friendly fuels as well as for the desire to be independent of mineral oil or its limitation in future [1–3]. Renewable energy sources seem to be a necessity for our rapidly rising global population. Biodiesel belongs to one of the most readily implemented and low cost renewable fuels for meeting the near future societal demands of transportation. It is already in use to some extent. There are a plenty of natural sources and biomass of different origin for producing biodiesel, including biomass from soybean, sunflower, rapeseed, coconut, palm oil, or nonfood sources of alga, lignocellulose, sugars, and triglycerides [4–8]. Current practices producing biodiesel are transesterification of plant oil, like soybean or rapeseed oils.

Commercial biodiesel is synthesised by liquid base catalysed transesterification of C_{10} – C_{20} tricylglyceride (TAG) components of lipids with C_1 – C_2 alcohols into fatty acid

methyl esters (FAMES) [9–14]. The acyl group chain of the esters produced normally ranges from 12 to 24 carbon atoms and the number of unsaturated bonds is up to 3. A possible by-product is glycerol [8, 13]. A major advantage of such transesterification routes is the possibility of localised fuel production, because processes typically operate at temperatures below 150°C that are more suitable for small scale production. Lee and Wilson [8] as well as Silva et al. [14] point to the fact that fuel quality is highly dependent on oil source. That is, chain length of the FAME molecules is influencing fuel properties such as cloud and pour points or long term stability against oxidation.

In the US, the quality of biodiesel is regulated by the ASTM D6751 (Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels). In European countries, the EN-14214 (automotive fuels, fatty acid methyl esters (FAMES) for diesel engines, requirements and test methods) regulates the biodiesel that allowed composition. Although there are specific standards for the biofuel quality, a lot of questions like biofuel performances and corrosive or tribological influences on materials need to be tested.

Ogunkoya et al. [15] investigate the effect of biodiesel on engine performance, combustion, and emissions. They compared traditional biodiesel and next generation biodiesel (NGBD). The NGBDs were produced by a two-step process: hydrolysis of oil into fatty acids and a thermocatalytic process to remove oxygen by a decarboxylation reaction. Engine performance, combustion, and emissions depend strongly on the type of biodiesel. Results from combustion showed shorter ignition delays for most of the renewable deoxygenated biodiesel. Combustion results also reveal lower peak in-cylinder pressure, reducing rate of increase in hydrocarbon emissions for the deoxygenated NGBDs. For fulfilling the demands of European standards for limitation of emissions like EU6, it is essential to consider changes in the emission of NO_x or hydrocarbons. Emission tests from Ogunkoya et al. [15] showed an increase in hydrocarbon emissions of the NGBDs but a general decrease in all other emissions including NO_x, greenhouse gases, and soot.

Not only fuel quality and efficiency but other properties of biodiesel need to be proven and evaluated before reliable usage in technical sensitive systems. Especially in sensitive powertrain applications, that is, the fuel injection system, the wear resistance of moving parts in the diesel environment is essential for reliable and long term durability. There are sensitive highly optimized coating systems in modern fuel pumps and injectors for cars. Pump and injector design rely on the diesel fuel lubrication [16–18]. Slight reduction in fuels lubricity can lead to numerous fuel injection failures with adhesive sliding wear and scuffing (serve adhesive wear) due to rapid loss of fuel lubrication performance.

Detailed knowledge of the impact and behaviour of different biodiesel or diesel/biodiesel blends on wear, friction, and long term durability of parts is useful and of importance for the materials and coating selection [14]. Furthermore, the selection of biodiesel or an improvement of its quality and specific recommendations for changing biodiesel composition before additive addition may be of general interest.

In this paper, two different kinds of biodiesel were tested in terms of their impact on wear resistance. The knowledge about the tribological behaviour of different types of biodiesel is rare. Rape and soybean are two of the most common natural sources for biodiesel production. However, there is still less information about their impact on wear of powertrain systems for transportation. The composition of biodiesel can change in quite a wide range. Although the quality of biodiesel seems to be similar and according to the demands, biodiesel from different natural origin could affect changes in the tribological behaviour under different conditions.

2. Experimental Methods

2.1. Coating Deposition by PECVD. Si-DLC as a part of multilayered surface design is a potential candidate coating for fuel pump and injector needle. Silicon doped hydrogenated diamond-like carbon was deposited by plasma enhanced chemical vapour deposition at the company PlasTec GmbH, Wuppertal. Si-DLC films were deposited in a

radio frequency rf PECVD chamber, whose base pressure was between 5.0 and 8.0 × 10⁻⁵ Pa. The plasma chamber contains two electrodes. The radio frequency power (13.56 MHz) was capacitive coupled to one of the cathodes. The substrates are flat disks of 100Cr6 (1.3505) with an outer diameter of 24 mm ± 0.5 mm and a height of 7.8 mm ± 0.1 mm and a hardness of 62 HRC ± 1 HRC.

2.2. Sliding Wear Tests. Wear tests were carried out in a translatory oscillation apparatus of the company Optimol Instruments GmbH, Munich. All tests were performed according to the standards DIN 51834-Part 1 (general working principles), DIN 51834-Part 2 (determination of friction and wear data for lubricating oils), and DIN 51834-Part 3 (determination of tribological behaviour of materials in cooperation with lubricants). With this equipment, the HFRR (high-frequency reciprocating rig) according to DIN EN ISO 12156-1 can be carried out also. The HFRR points attention to the fuels lubricity, only, while in the present study the whole tribological system is investigated under different conditions. Tests according to the standards DIN 51834 can be carried out at different temperatures, under different loads, frequencies of motion, and strokes in the translatory oscillation apparatus of the company Optimol Instruments GmbH, Munich. Friction coefficient was monitored continuously. The mentioned standards describe test methods based on a high-frequency, linear-oscillation test machine to determine tribological quantities like friction, wear, load carrying capacity, and extreme pressure behaviour of liquid lubricants and consistent lubricants in the ball-on-disk contact geometry [19].

The test ball is made of 100Cr6H. The disk (flat) consists of 100Cr6H as well. It is used with an uncoated or with a diamond-like carbon coated surface. Test frequency is 10 Hz. Stroke length (single sliding path of one oscillation) amounts to 1000 μm. A normal load of 10 N was applied for a testing time of 120 min. Before testing, the surface of ball and flat were cleaned with alcohol. Wear tests were carried out at room temperature and at 150°C. For the present study, two different kinds of biodiesel were chosen as lubricants. Furthermore, tests were carried out without lubricant (dry condition) at room temperature as well as at 150°C. Each test was carried out with a new ball, while the coated flat sample was used for several tests, but in different areas.

Consistent with DIN 51834-Part 3, the volumetric wear of the ball (Figure 1) was determined according to

$$W_{V,BALL} = \frac{\pi \cdot d_1^2 \cdot d_2^2}{64} \left[\frac{1}{R} - \frac{1}{\bar{R}} \right], \quad (1)$$

where $W_{V,BALL}$ is volumetric wear of the ball, d_1 is wear trace diameter on the ball surface parallel to the oscillation direction, d_2 is wear trace diameter on the ball surface perpendicular to the oscillation direction, \bar{R} is average radius of the worn ball area after the test, and R is radius of the ball before the test.

The planimetric wear amount of the flat sample $W_{q,FLAT}$ was measured in the centre of the wear trace perpendicular to the sliding direction according to DIN 51834-3:2008. The

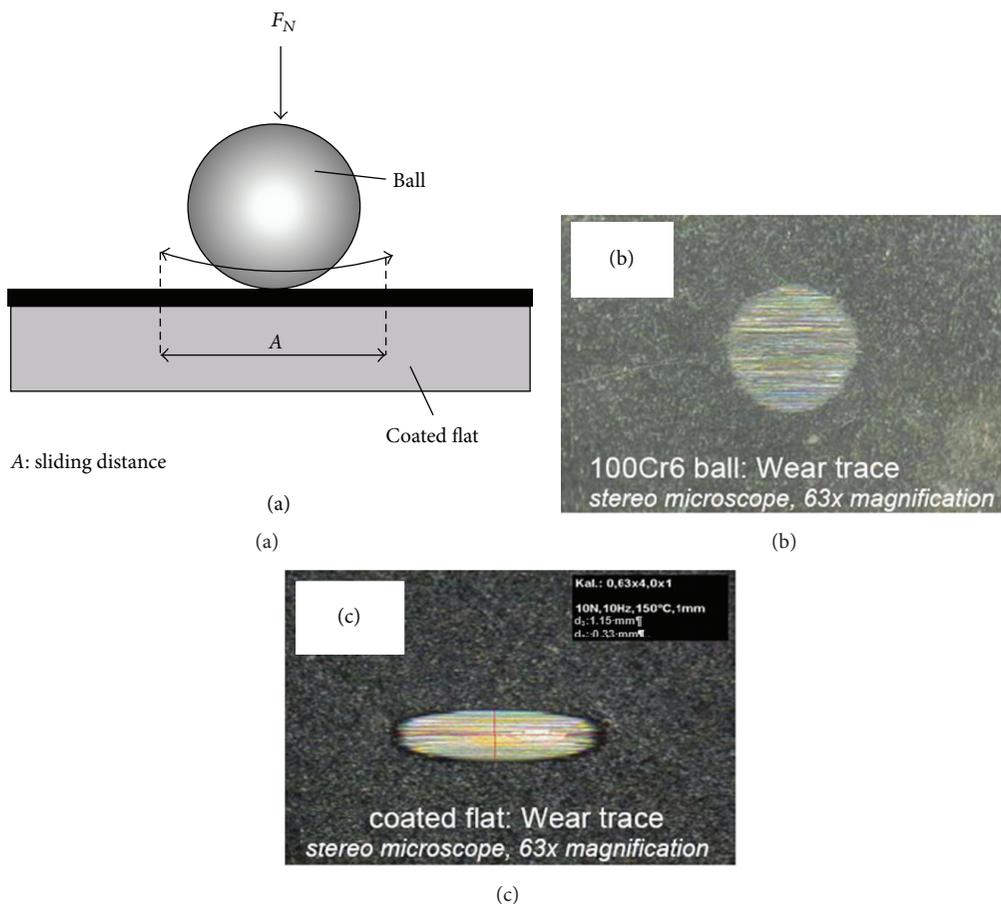


FIGURE 1: Wear test setup according to DIN 51834-Part 1 (a), wear trace in the ball (b), and wear trace in the flat disk (c).

volumetric wear of the flat is calculated from the planimetric wear amount $W_{q,FLAT}$ of the wear trace according to

$$W_{V,FLAT} = \frac{\pi \cdot d_4^2 (d_3 - s)^2}{64} \cdot \frac{1}{\bar{R}} + s \cdot W_{q,FLAT}, \quad (2)$$

where $W_{V,FLAT}$ is volumetric wear of the flat sample, d_3 , d_4 are cross-section of the wear trace within the flat parallel and perpendicular to the sliding direction with $d = 0.5(d_3 + d_4)$, s is stroke length, and $\bar{R} = d_4^3 / 12W_{q,FLAT}$ ($d_4 = d_2$).

The total wear rate is calculated by the sum of $W_{V,BALL}$ and $W_{V,FLAT}$ correlated to the whole sliding distance and the chosen normal force.

2.3. Characterization of Biodiesel. In the present study, two different natural sources for gaining plant oil and, subsequently, processing biodiesel by transesterification were used: soya and rape. The two kinds of biodiesel, rapeseed methyl ester (RME) and soybean methyl ester (SME), were applied as intermediate liquid in the wear tests with and without oxidation stabilizer. As oxidation stabilizer, 2,2'-methylenebis(6-tert-butyl-4-methylphenol), $C_{23}H_{32}O_2$ (Figure 2), was used. The concentration of the oxidation stabilizer in the biodiesel RME or SME is shown in Table 1. In Table 2, a selection of

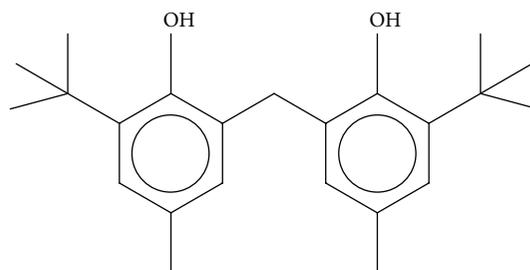


FIGURE 2: Chemical structure of oxidation stabilizer 2,2'-methylenebis(6-tert-butyl-4-methylphenol), $C_{23}H_{32}O_2$, CAS Registry Number 119-47-1.

test according to DIN EN 14214:12-11, which was performed with the biodiesel fuels, is summarized. The biodiesel was supplied by the company ASG Analytik-Service Gesellschaft mbH Neusäss.

2.4. Scanning Electron Microscopy (SEM). Scanning electron microscopy was carried out on all wear. The SIGMA Series of ZEISS EVO MA15 Field Emission Scanning Electron Microscope (FE-SEM) is equipped with the GEMINI column. Its in-lens secondary electron detection brings an unparalleled

TABLE 1: Fraction of oxidation stabilizer in RME and SME biodiesel.

Biodiesel	w/o oxidation stabilizer	200 mg/kg oxidation stabilizer $C_{23}H_{32}O_2$	1000 mg/kg oxidation stabilizer $C_{23}H_{32}O_2$
Rapeseed methyl ester	RME w/o OS	RME 200 OS	RME 1000 OS
Soybean methyl ester	SME w/o OS	SME 200 OS	SME 1000 OS

OS: oxidation stabilizer $C_{23}H_{32}O_2$.

TABLE 2: Selection of tests for biodiesel characterization according to DIN EN 14214:12-11.

Feature	Standardized testing method
Ester content	DIN EN 14103
Total glyceride content	DIN EN 14105
Sulphur content	DIN EN ISO 20884
Cetane content	DIN EN 15195
Water content	DIN EN ISO 12937
Copper corrosion	DIN EN ISO 2160
Oxidation stability	DIN EN 14112
Acid number	DIN EN 14104

resolution. The images were recorded using the detection mode of secondary electrons.

3. Results and Discussions

3.1. Characterization of Biodiesel. Ester content of rapeseed methyl ester with and without oxidation stabilizer was measured to be >99%. Biodiesel from soybean methyl ester had an ester content of >98.1% according to DIN EN 14103. Total glyceride content of RME biodiesel is 0.1% without and with oxidation stabilizer. For all SME, the glyceride content is double as high as in RME and amounts to 0.2%.

As expected, with the addition of oxidation stabilizer $C_{23}H_{32}O_2$, the oxidation resistance determined according to DIN EN 14112 increases. DIN EN 142214:12-11 demands a minimum value of 8 h oxidation resistance. Without oxidation stabilizer neither RME nor SME can fulfil this requirement. RME without oxidation stabilizer has a stability up to 7.3 hours, while SME even has a lower stability of 4.5 hours without the addition of $C_{23}H_{32}O_2$ only. For both kinds of biodiesel, the oxidation stability increases with the addition of the stabilizer $C_{23}H_{32}O_2$. Increasing fraction of $C_{23}H_{32}O_2$ results in a further improved oxidation stability. Adding 200 mg/kg oxidation stabilizer $C_{23}H_{32}O_2$ effects an oxidation resistance of 12.5 hours for RME and of 6.4 hours for SME. 1000 mg/kg oxidation stabilizer $C_{23}H_{32}O_2$ results in an oxidation stability of 24.5 hours for RME and 12.5 hours for SME. In general, the used SME has a minor lower oxidation stability in comparison to RME (Figure 3).

Both kinds of biodiesel have different water content. The effect of the presence of water in diesel fuel on the wear resistance is well known [20–22]. Water and the existence of oxygen in the water favour abrasion and corrosion. Iron oxides like hematite Fe_2O_3 and magnetite Fe_3O_4 were formed on the metal surface during the energy input due to the ongoing sliding motion. The iron oxides contribute to destroying

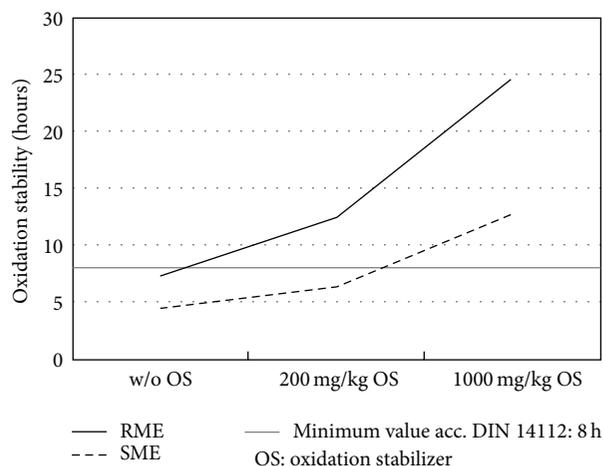


FIGURE 3: Oxidation stability of RME and SME biodiesel in dependence on the concentration of oxidation stabilizer $C_{23}H_{32}O_2$.

the lubrication film on the rubbing surfaces and promoting scratching. Lapuerta et al. [22] point to the fact that biodiesel is more hydrophilic and shows higher hygroscopy than fossil fuels. Hygroscopy is the ability to adsorb water from the surrounding air. The aromatic compounds in the fossil diesel fuel have a lower affinity for water than that of alkanes, mostly composed of synthetic diesel fuels [23, 24]. Fatty acid methyl esters with polar chemical structure of carboxyl groups have a much stronger ability to absorb moisture [25]. In general, high water content in diesel is negative, because it decreases lubricity, causes biological growth which modifies fuel composition, and lowers its quality [26]. The water content is limited to maximum values of 500 ppm for biodiesel fuels and 200 ppm for fossil diesels. The two kinds of biodiesel tested in this study fulfil the demands of the standard DIN EN ISO 12937. However, there are clear differences in the water content of rapeseed methyl ester and soybean methyl ester biodiesel. The three tests RME with and without oxidation stabilizer have a water content of 64 mg/kg. SME biodiesel contains double of the water content in comparison to RME. All kinds of SME biodiesel have a water content of 127 mg/kg. For all biodiesel, the water content or the ability to absorb water does not change in dependence on the addition of oxidation stabilizer $C_{23}H_{32}O_2$. Differences in the biodiesel ability to absorb moisture in the present study may be caused by its different structure. The ability to absorb water may change in dependence on the chain length of the methyl esters as well as on the unsaturation degree. Selected data from the biodiesel analyses are summarized in Table 3.

TABLE 3: Selected results from biodiesel analyses according to DIN EN 14214:12-11.

Feature	Limits acc. standards	RME w/o OS	RME 200 mg/kg OS	RME 1000 mg/kg OS	SME w/o OS	SME 200 mg/kg OS	SME 1000 mg/kg OS
Ester content	96,5%	>99%	>99%	>99%	98,1%	98,1%	98,1%
Total glyceride content	max. 0.25%	0.1%	0.1%	0.1%	0.2%	0.2%	0.2%
Sulphur content	max. 10 mg/kg	<5 mg/kg	<5 mg/kg	<5 mg/kg	<5 mg/kg	<5 mg/kg	<5 mg/kg
Cetane index	min. 51.0	52.5	52.5	52.5	57.1	57.1	57.1
Water content	500 mg/kg	64 mg/kg	64 mg/kg	64 mg/kg	127 mg/kg	127 mg/kg	127 mg/kg
Copper corrosion	1	1	1	1	1	1	1
Oxidation stability	min. 8 h	7.3 h	12.5 h	24.5 h	4.5 h	6.4 h	12.5 h
Acid number	max. 0.5 mg KOH/g	0.49 mg KOH/g	0.49 mg KOH/g	0.49 mg KOH/g	0.271 mg KOH/g	0.217 mg KOH/g	0.217 mg KOH/g

TABLE 4: Total wear rate of 100Cr6 steel against Si-DLC coated flat in different biofuels at room temperature or 150°C.

Intermediate condition	Total wear rate at room temperature ($\times 10^{-7}$ mm ³ /Nm)	Total wear rate at 150°C ($\times 10^{-7}$ mm ³ /Nm)
Dry (w/o biodiesel*)	16.9 \pm 1.2	203.0 \pm 5.5
RME w/o oxidation stabilizer C ₂₃ H ₃₂ O ₂	4.9 \pm 0.3	16.5 \pm 0.4
RME 200 mg/kg oxidation stabilizer C ₂₃ H ₃₂ O ₂	8.7 \pm 0.8	20.3 \pm 1.2
RME 1000 mg/kg oxidation stabilizer C ₂₃ H ₃₂ O ₂	14.6 \pm 1.3	28.0 \pm 1.4
SME w/o oxidation stabilizer C ₂₃ H ₃₂ O ₂	3.6 \pm 0.1	32.5 \pm 3.4
SME 200 mg/kg oxidation stabilizer C ₂₃ H ₃₂ O ₂	4.0 \pm 0.1	34.2 \pm 2.5
SME 1000 mg/kg oxidation stabilizer C ₂₃ H ₃₂ O ₂	4.5 \pm 0.3	35.2 \pm 0.8

* At room temperature under ambient air.

3.2. *Sliding Wear Tests: Wear Rate.* After 120 min sliding of 100Cr6 ball against the Si-DLC coated surface without diesel addition, the total wear rate amounts to $16.9 \pm 1.2 \times 10^{-7}$ mm³/Nm at room temperature. At 150°C, the wear rate is more than 10 times higher and reaches $203 \pm 5.5 \times 10^{-7}$ mm³/Nm (Table 4). Figures 4 and 5 show the results from translatory oscillation tests. It is evident that biodiesel acts as lubricant at room temperature and at 150°C. For sliding tests of 100Cr6 ball against Si-DLC flat in rapeseed methyl ester without oxidation stabilizer, the wear rate is reduced to $4.9 \pm 0.3 \times 10^{-7}$ mm³/Nm. This is about one-third in comparison to the tribological system 100Cr6 against Si-DLC without biodiesel. The addition of oxidation stabilizer C₂₃H₃₂O₂ is necessary to make biodiesel more stable and enable using other longer periods of time after production or even handling in contact with metallic surfaces, which have a catalytic effect mostly. As tested in this study and illustrated before (Figure 3), the addition of stabilizer C₂₃H₃₂O₂ improves the oxidation resistance of RME and SME. However, it is evident from sliding wear tests that the wear rate is negatively influenced by the oxidation stabilizer. The addition of 200 mg/kg oxidation stabilizer C₂₃H₃₂O₂ leads to a wear rate of $8.7 \pm 0.8 \times 10^{-7}$ mm³/Nm for rapeseed methyl ester. If 1000 mg/kg C₂₃H₃₂O₂ is added to RME, the

oxidation stability is best, but the wear rate almost reaches the value of non-biodiesel lubricated conditions 100Cr6 ball against Si-DLC flat. For soybean methyl ester the influence of oxidation stabilizer C₂₃H₃₂O₂ on the wear rate is less strong at room temperature. Already without any stabilizer C₂₃H₃₂O₂, 120 min sliding of 100Cr6 ball against Si-DLC flat in soybean methyl ester results in the lowest wear rate of $3.6 \pm 0.1 \times 10^{-7}$ mm³/Nm in this study. However, a minor increase of the wear rate is measured in dependence on the addition of oxidation stabilizer C₂₃H₃₂O₂ as well as for SME. The wear rate amounts to $4.5 \pm 0.3 \times 10^{-7}$ mm³/Nm for 100Cr6 against Si-DLC in SME with 1000 mg/kg C₂₃H₃₂O₂.

At 150°C, the tribological behaviour is different. Soybean oil based biodiesel leads to a higher wear rate in comparison to rapeseed methyl ester (Table 4, Figure 5). There are only small differences in SME w/o oxidation stabilizer and SME with C₂₃H₃₂O₂. w/o oxidation stabilizer of the wear rate is $32.5 \pm 3.4 \times 10^{-7}$ mm³/Nm. If SME contains 200 mg/kg oxidation stabilizer, the wear rate amounts to $34.2 \pm 2.5 \times 10^{-7}$ mm³/Nm. In the case of the application of 1000 mg/kg oxidation stabilizer in SME, the wear rate is still $35.2 \pm 0.8 \times 10^{-7}$ mm³/Nm. Wear rate of rapeseed methyl ester w/o C₂₃H₃₂O₂ is $16.5 \pm 0.4 \times 10^{-7}$ mm³/Nm. It remains about half as high as SME wear rate with and w/o oxidation stabilizer. A

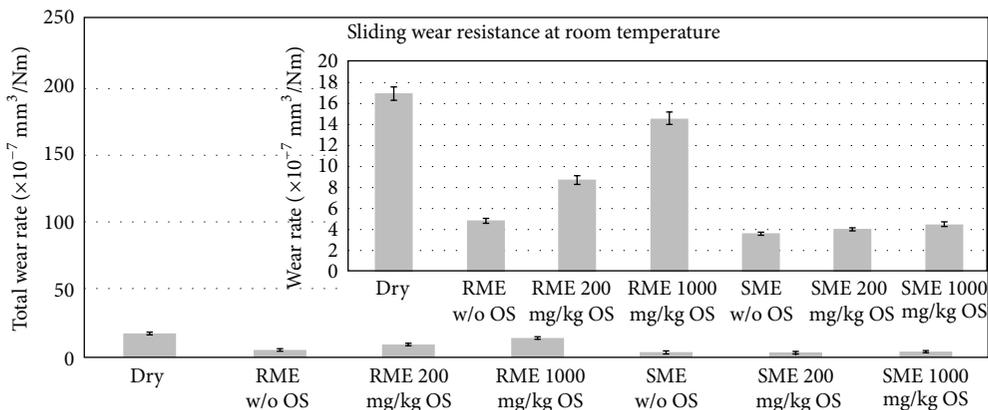


FIGURE 4: Results from translator oscillation tests at room temperature (100Cr6 steel ball against Si-DLC flat). Scaling of the y-axis is different for better comparison to Figure 5.

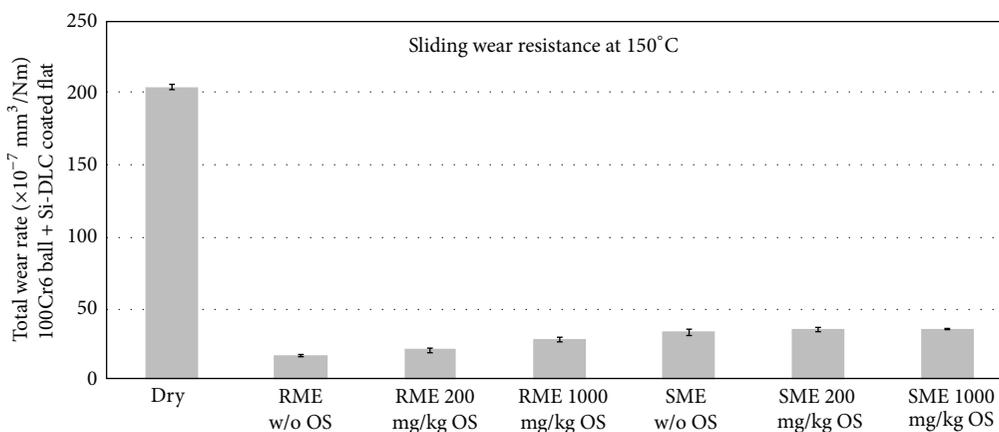


FIGURE 5: Results from translator oscillation tests at 150°C (100Cr6 steel ball against Si-DLC flat).

straight increase of RME wear rate with addition of oxidation stabilizer can be measured at 150°C as well.

3.3. Sliding Wear Tests: Friction Coefficient in Ambient Air. Further information can be gained by evaluating the coefficients of friction. Variations of coefficient of friction versus the relative humidity for different silicon concentrations in a DLC coating were reported [27–32]. The coefficients of friction depend on the moisture and the silicon content strongly. The typical interaction of Si-DLC with moisture and suitable functional groups is promoted by energy input due to sliding and tribochemical effects. SiO_2 wear debris was found in the worn surfaces. SiO_2 is favoured to absorb polar groups like $-\text{OH}$ -groups from humidity, water, or other components of the diesel. This behaviour results in the formation of Si-O-OH sol-gel-transfer film with low friction. When sliding in humid environments Si-DLC forms a sol-gel layer containing Si-O attracting polar functional groups. Si and O, $-\text{OH}$, and other functional groups are detected in the worn areas of Si-DLC by FT-IR, which is attributed to the presence of this silica-sol layer.

Figures 6 and 7 show the friction coefficient without lubrication by biodiesel at room temperature and at 150°C.

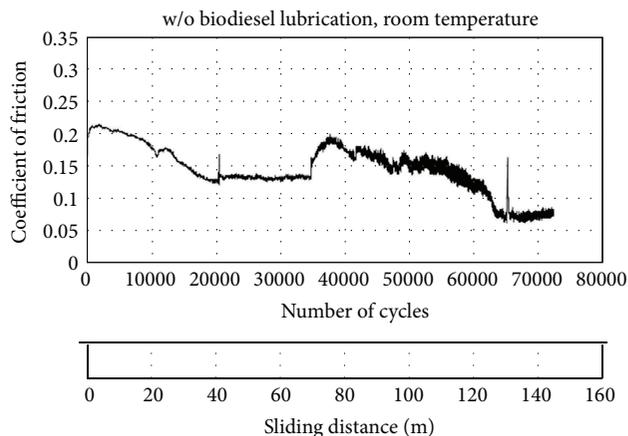


FIGURE 6: Friction coefficient in ambient air at room temperature (100Cr6 steel ball against Si-DLC flat).

As mentioned before, the tribological behaviour is attributed to the formation of Si-O-OH sol-gel-transfer layer in the presence of humidity or suitable functional groups. Without biodiesel, these advantageous properties cannot or at least not fully develop.

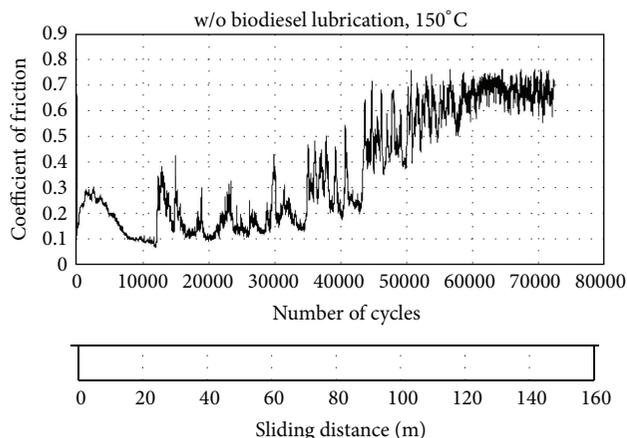


FIGURE 7: Friction coefficient in ambient air at 150°C (100Cr6 steel ball against Si-DLC flat).

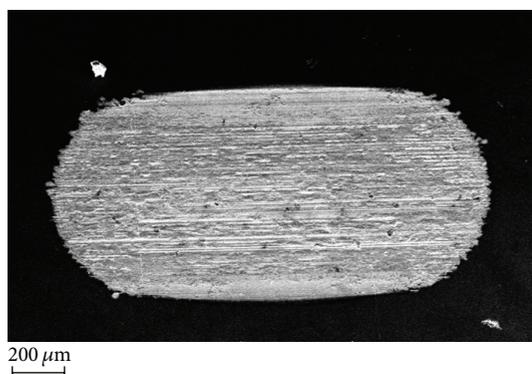


FIGURE 8: SEM image of worn surface of Si-DLC coated flat after tribological testing against 100Cr6 ball at 150°C in ambient air (dry).

For RME, at room temperature, interaction with the humidity of the ambient air and environment is sufficient to reduce the friction coefficient even down to below 0.1 after 70000 cycles (140 m sliding distance), Figure 6. At 150°C testing temperature, the humidity at the tribological loaded contacts evaporates quickly. Under this dry atmosphere in the sliding contact, Si-DLC cannot develop its favourable low friction potential. The coefficient of friction grows drastically to around 0.7 after 70000 cycles (140 m sliding distance), Figure 7. After the tribological test at 150°C in ambient air (dry), the Si-DLC is worn away. As shown by SEM (Figure 8), the metallic 100Cr6 substrate is exposed.

Hioki et al. [33] observed transfer film formation on Si-DLC composed of C : Si : O with composition 0.8 : 0.1 : 0.1 and 10% of hydrogen under humid conditions. When sliding in a dry atmosphere, there is only carbonaceous debris in the wear trace [31, 32].

Oguri and Arai [32] point out further that, for dry behaviour, the friction and wear behaviour of undoped hydrogenated DLC cannot be surpassed, whatever the contact pressure. However, for humid condition, under delivering of polar functional groups and low contact pressures (<1 GPa), using Si-DLC for applications requiring both low

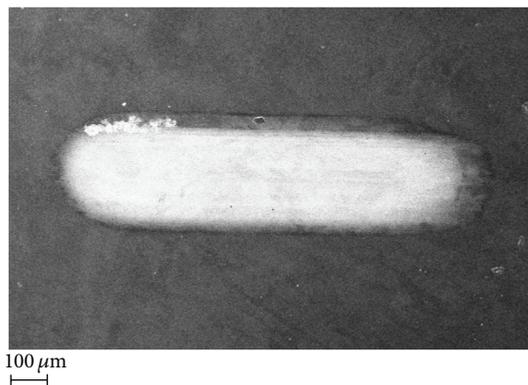


FIGURE 9: SEM image of worn surface of Si-DLC coated flat after tribological testing against 100Cr6 ball at 150°C in biodiesel (soybean methyl ester, SME).

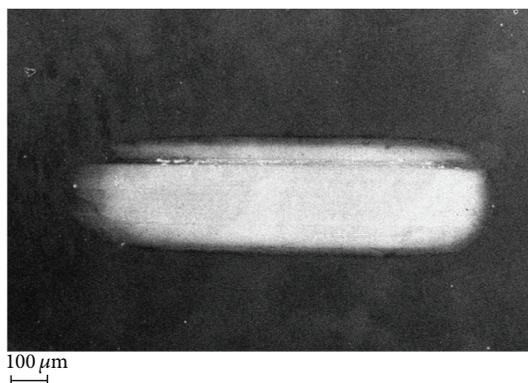


FIGURE 10: SEM image of worn surface of Si-DLC coated flat after tribological testing against 100Cr6 ball at 150°C in biodiesel (rapeseed methyl ester, RME).

friction (<0.1) and high wear resistance (10^{-7} mm³/Nm) is recommended.

3.4. Sliding Wear Tests: Friction Coefficient in Biodiesel. Biodiesel reduces the wear significantly. Figures 9 and 10 show the wear traces in Si-DLC coated flats after tribological testing in SME or RME, both w/o oxidation stabilizer. It is seen that the Si-DLC coating was not worn away in both cases, if biodiesel lubricates. This result correlates with the reduced wear rates (Table 4) for biodiesel lubrication.

Several authors report [34–36] that biodiesel that contains high fraction of oxygen (O) and increased number of ester groups can reduce the wear and friction between contact surfaces given the presence of aliphatic fatty acid. This fatty acid enhances lubrication property by developing lubricating soap films. Havet et al. [36] report that the length of the fatty acid chain thickens the film and thereby increases the area of the protected surface.

The friction coefficient is around 0.15 after running in time for soybean methyl ester. For RME, the friction coefficient even lowers down to ultralow values of 0.06 (Figure 11)

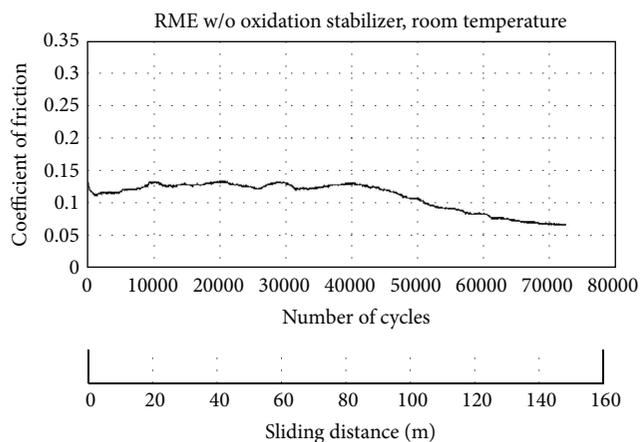


FIGURE 11: Ultralow friction with Si-DLC in rapeseed methyl ester w/o oxidation stabilizer at room temperature after 50000 cycles (100 m sliding distance) (100Cr6 steel ball against Si-DLC flat).

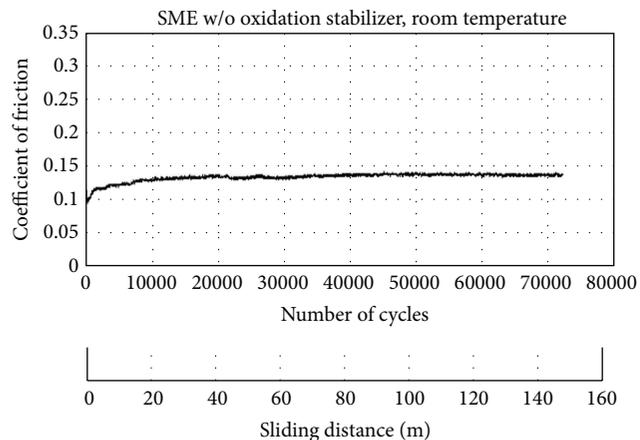


FIGURE 12: Friction coefficient in biodiesel w/o oxidation stabilizer: SME w/o OS, room temperature (100Cr6 steel ball against Si-DLC flat).

at around 70000 cycles (140 m sliding distance) at room temperature. With oxidation stabilizer 2,2'-methylenebis(6-tert-butyl-4-methylphenol), $C_{23}H_{32}O_2$, such ultralow friction was not observed.

The type of feedstock and the kind of plant oil used for the biodiesel production seem to be essential for its influence on the tribological behaviour. In the present study, at room temperature, the RME biodiesel effects a higher wear rate in comparison to biodiesel produced from soybean oil.

During lubrication with SME at room temperature, the friction coefficient stays stable without any abrupt alterations, Figure 12. At 150°C, sudden changes in the friction coefficient were recorded for SME without and with oxidation stabilizer. Figure 13 illustrates this observation. On the contrary, the friction coefficient stays stable for RME at 150°C (Figure 14). Figures 15 and 16 show SEM images of the wear traces on the Si-DLC coated 100Cr6 flat at 150°C in SME or RME. In both cases, the Si-DLC coatings are still present in the wear trace.

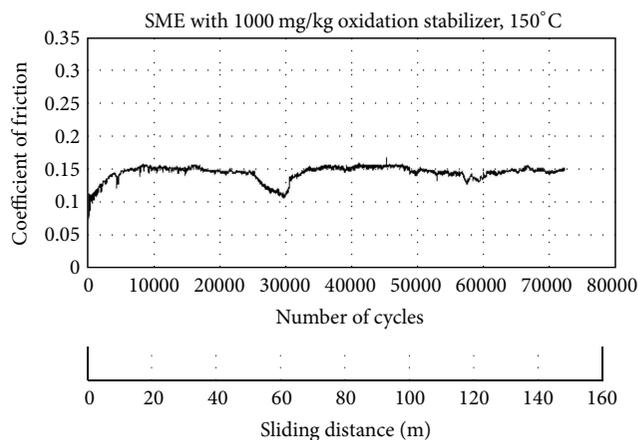


FIGURE 13: Friction coefficient in biodiesel with 1000 mg/kg oxidation stabilizer: SME with OS, 150°C (100Cr6 steel ball against Si-DLC flat).

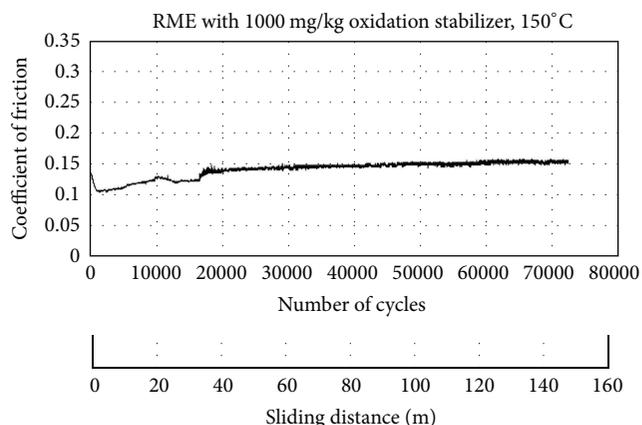


FIGURE 14: Friction coefficient in biodiesel with 1000 mg/kg oxidation stabilizer: RME with OS, 150°C (100Cr6 steel ball against Si-DLC flat).

Water content in soybean methyl ester biofuel is about double as high as in rapeseed methyl ester in the received conditions. In general water content in fuel strongly reduces lubricity [22]. However, Si-doped diamond-like carbon needs the functional groups of dissociated water for stable low friction. At 150°C, water may desorb and mostly important free water starts to disappear. It starts to evaporate. This process may be supported by the large surface of the thin lubricating biodiesel film on the Si-DLC flat samples. The proposed mechanism of water desorption on evaporation is more or less additionally activated by the accumulated energy due to the sliding motion. This mechanism may not be homogeneous. Sudden changes of the frictional situation, as seen in Figure 14, may result in inhomogeneous distribution of water and other easily desorbing functional groups.

It is worth mentioning that the presence of small amounts of water in the fuel, if stable and controlled, can have a positive effect on the physical and chemical kinetics of combustion, whereby it reduces combustion temperatures and provides OH radicals in the combustion environment [37, 38]. The OH



FIGURE 15: SEM image of worn surface of Si-DLC coated flat after tribological testing against 100Cr6 ball at room temperature, RME w/o OS.

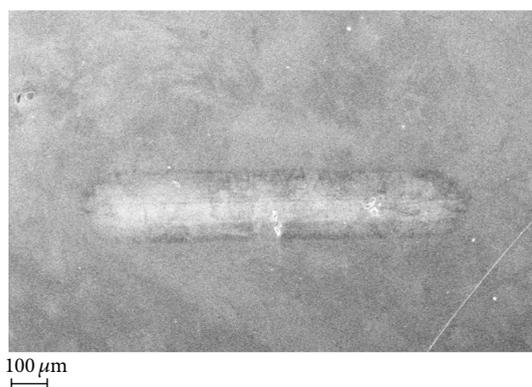


FIGURE 16: SEM image of worn surface of Si-DLC coated flat after tribological testing against 100Cr6 ball at room temperature, SME w/o OS.

radicals control NO_x formation and oxidative soot resulting in reducing both NO_x and particle emissions. Microexplosion actions of water droplets contribute as an essential mechanism to improved distribution of fuel and oxidants, causing more complete combustion and consequently a significant reduction of criteria pollutants emissions, when using water-containing fuels [37–39].

Geller and Goodrum [40] report that FAME obtained from vegetable oil showed better performance as lubricity enhancing additives than did their single fatty acid based counterparts. FAME composition has an influence on the lubricity enhancing properties, but vegetable oil based FAMES have an additional factor effecting lubricity which is not active in pure FAMES. Features such as saturation, chain length, and hydroxylation influence the performance of the FAMES obtained from vegetable oils as lubricity enhancers. FAMES which contain hydroxylated fatty acids are more effective lubricity improvers in comparison to their nonhydroxylated analogues. Soybean based biodiesel provides unique chemical properties due to its hydroxyl functionality at room temperature. The hydroxyl group is significant because it facilitates plasticization and adhesion of the oil esters, properties which are useful in a variety

of applications such as plastics, inks, and adhesives [28]. This functionality may also be useful to increase lubricity associated with FAMES [27, 29].

The composition, stability, and surfactants and additive selection for clean and efficient and optimal lubricating biodiesel are an important field of future research.

4. Conclusions

4.1. Oxidation Stabilizer. It was observed for both test types of biofuels, rapeseed methyl ester or soybean methyl ester, that increasing amount of oxidation stabilizer 2,2'-methylenebis(6-tert-butyl-4-methylphenol), C₂₃H₃₂O₂, promotes the friction and the wear. Oxidation stabiliser saturates double bonds. It may be reducing the stability or the amount of functional groups at the Si-DLC surface, whereby the formation of the necessary lubricating Si-O- sol-gel transfer layer could be prevented.

4.2. Operating Conditions for Si-DLCs in Biodiesel. Si-DLCs with optimized structure may be the coating of choice for operating in biodiesel, which promotes the formation of Si-O-OH sol-gel-transfer film with low or ultralow friction. Biodiesel contains humidity and plenty of polar functional groups. As Si-DLC usually has lower hardness in comparison to undoped DLC variants, care needs to be taken for optimal contact conditions. Therefore, low contact pressure (<1 GPa) is a second precondition for applying Si-DLC successfully. Using Si-DLC in applications having a humid atmosphere with polar functional groups and requiring both low friction (<0.1) and high wear resistance (<10⁻⁷ mm³/Nm) is recommended.

4.3. Addition or Natural Generation of Surfactants. If silicon doped diamond-like carbon coatings were used for powertrain components in contact with biodiesel, water content may be favourable for formation of a lubricating Si-O-OH sol-gel film. However, the distribution of the water needs to be homogeneous in the lubricating fuel. The addition of surfactants, which guarantee a homogeneous and stable emulsion of diesel and water, may be favourable. Coalescence mechanisms of the water could lead to interruption of the Si-OH film with minor or no water content, by this lowering the lubricity.

Competing Interests

The authors declare that they have no competing interests.

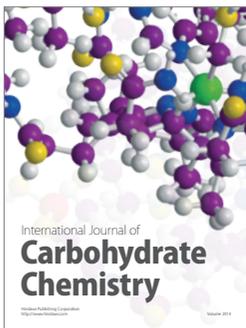
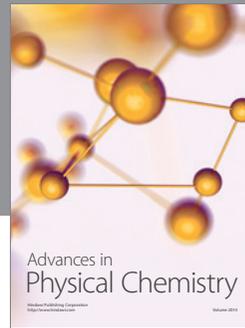
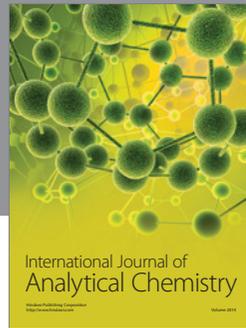
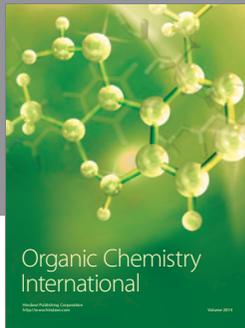
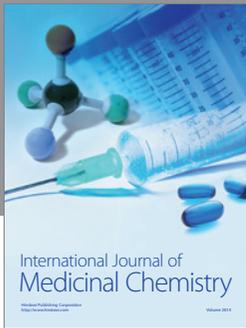
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