

Diesel Lubricity Requirements of Future Fuel Injection Equipment

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ABSTRACT

This paper looks at the underlying fundamentals of diesel fuel system lubrication for the highly-loaded contacts found in fuel injection equipment like high-pressure pumps. These types of contacts are already occurring in modern systems and their severity is likely to increase in future applications due to the requirement for increased fuel pressure.

The aim of the work was to characterise the tribological behavior of these contacts when lubricated with diesel fuel and diesel fuel treated with lubricity additives and model nitrogen and sulphur compounds of different chemical composition. It is essential to understand the role of diesel fuel and of lubricity additives to ensure that future, more severely-loaded systems, will be free of any wear problem in the field.

The lubricity with the High-Frequency Reciprocating Rig (HFRR) and the critical load of incipient scuffing (load-carrying capacity) in the High-Temperature Oscillating Machine (HiTOM) using real components of a Common Rail (CR) pump as test samples depends on the composition of the base fuels. A content of 5 % rapeseed-methyl ester (RME) in fuel increases the load-carrying capacity and increases the lubricity. Hydrodesulphurization decreases the lubricity of gas oil by 80 - 200 μm and the load-carrying capacity by 1500 N. Model sulphur compounds benzothiophene, dibenzothiophene and 4,6-dimethyldibenzothiophene cannot restore the lubricity of a hydrotreated diesel fuel, but can increase the load-carrying capacity. The model

nitrogen compound 8-hydroxyquinoline improves the lubricity at very low concentrations (20 ppm nitrogen) whereas quinoline and acridine need a higher concentration (100 ppm nitrogen) for some lubricity improvement.

The outcome of this work has confirmed that specific lubricity additive chemistries can stretch the mixed lubrication area where highly-loaded contacts can operate safely. Specific lubricity additives with carboxylic acid-, ester- and amide based chemistries can increase the lubricity in a variety of base fuels at a concentration of 200 ppm to meet the lubricity requirement according to EN 590. These compounds can provide protection against adhesive wear by increasing the incipient scuffing load. Higher than market-typical additive concentrations can further increase lubricity, but are levelling at concentrations between 1000 ppm and 2000 ppm. The ester-based additives level at a lower value than the acid and amide based additives and so can provide further protection to FIEs. The load-carrying capacity of test fuel - ULSD 1 - can be increased by 4500 N by an ester content of 1000 ppm. The acid can only provide an increase of 2500 N. The ester-based additive at 200 ppm can already provide an improvement of the load-carrying capacity by 3000 N at a fuel temperature of 90 °C.

Tribological investigations with the HiTOM showed an excellent correlation between the results of this test and the HFRR results.

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INTRODUCTION

The composition of diesel fuel has a strong impact on the wear of fuel injection equipment and model wear specimen in tribological test rigs [1,2]. The adverse effect of severely hydrodesulphurized diesel fuel on distributor type injection pumps has been pointed out in several studies [2-6]. In order to restore the lubricity of hydrotreated diesel fuels, several different types of lubricity additives have been developed and are added to the fuel. These additives are added to the base fuel together with other additives, e.g. detergents, defoamers and cold flow additives. It has been confirmed in field tests that a careful selection of the additive technology can completely restore the level of protection needed to ensure proper field operations without failure and performance loss due to wear [7,8]. Furthermore it has also been emphasized that the chemistry has to be carefully selected to avoid negative interactions with other additives that may lead to injector deposits or increase in cylinder bore polish [9,10].

Fuel injection equipment (FIE) systems for Euro 5 and beyond will have to generate extremely high fuel pressure and controlled injection events to meet stringent emissions legislations [11]. Such performance will be required for the effective life of the vehicles, ranging from 150 to 500 thousand kilometres for passenger cars depending on their application. It is therefore imperative that the FIE systems maintain their top performance during the entire life of the vehicle. In order to achieve this, new contacts and materials are being considered. At the same time new fuels are appearing in the market place that could have an impact on the performance of such FIE systems like fuels containing 10 ppm sulphur and fatty acid methyl ester (FAME) as a blend component. These new fuels are likely to increase the overall severity for the FIE environment. The best combination of new FIE contacts for Euro 5 type and beyond, fuels and fuel additives is one way to ensure that the goal of meeting future more stringent emissions legislation can be met without field issues.

MAIN SECTION

1. OBJECTIVE OF THE TEST WORK

Modern diesel engine cars are no longer equipped with distributor type fuel pumps. Instead, Common Rail fuel injection systems are used which allow the car manufacturers to meet more stringent noxious emission limits [12]. In the future, more restrictive emission legislations will put even greater demands for performance and durability on FIE which may result in more severe tribological conditions leading to higher fuel temperatures in the FIE and higher contact pressures. Although the HFRR test (see Chapter 4.2) is a suitable test for the assessment of fuel lubricity today, it does not provide information about the lubricating operational

limits of diesel fuel as the lubricant of future more advanced and highly stressed FIE (e.g. its load-carrying capacity). Therefore, the objective of this investigation was to:

- increase the knowledge of the tribological behaviour and the failure mechanism of different fuel compositions in a highly-loaded contact. This will provide information on whether current fuels and lubricity additives can provide wear protection under more severe tribological conditions.
- assess whether the HFRR test has the potential to reproduce these more severe tribological conditions.

2. EXPERIMENTAL SETUP

2.1 BASE FUELS AND ADDITIVES

Base fuels

In this work four different commercial base fuels have been tested. All fuels are free of any additive and their characteristics are listed in **Table 5** (Appendix). They include two ultra-low sulphur diesel fuels (ULSD 1, ULSD 2), one ULSD with a biodiesel content of 5 % (Rapeseed-Methyl Ester or RME) and one Swedish Class I diesel fuel (Class I). The Class I fuel contains an antistatic additive as this is routinely added to the fuel during production. Beside these fuels, three gas oils have also been tested (Appendix Table 6). These samples were taken from the gas oil product stream that feeds the hydrodesulphurization (HDS) plant, hence have relatively high sulphur content - and from the stream coming out of this plant that have very low sulphur content. Hydrotreated gas oil, the refinery term for middle distillate petroleum fractions, is the main blending component of diesel fuel. The light gas oil (LGO), medium gas oil (MGO) have been provided by a German refinery and the gas oil (GO) has been provided by a different German refinery. These samples differ by their boiling range (LGO 5 % volume evaporated distillation at 180 °C and 95 % at 300 °C; MGO: 5 % at 200 °C and 95 % at 360 °C; GO: 5 % at 211 °C and 95 % at 358 °C) and their kinematic viscosity (LGO 1.6 mm²/s; MGO 3.3 mm²/s; GO 2.8 mm²/s at 40 °C).

Lubricity additives

The typical chemical structure of a lubricity additive consists of a polar functional group attached to an oleophilic part R_i . Typical functional groups are carboxylic acid (Acid), carboxylic acid ester (Ester) and carboxylic acid amide (Amide) (Table 1). An ester for northern regions has also been tested that has the same functional group as the regular ester, but with a different oleophilic part for an increased solubility in diesel fuel at cold temperatures (high solubility ester - Hi.Sol.Ester). The market-typical treat rates of these additives to

achieve the required lubricity of 460 μm in an ULSD range from 50 ppm to 300 ppm. For our investigations four different commercial lubricity additives were selected. They comprise an acid, an ester, an ester designed for regions with extremely cold climates and an amide. All the lubricity additives tested do not contain any other active chemical, like detergents and cetane improver.

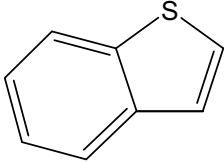
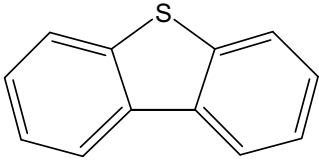
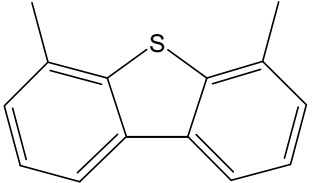
Table 1: Functional groups of lubricity additives [12]

Carboxylic acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}_1-\text{C}-\text{OH} \end{array}$
Carboxylic acid ester	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}_2-\text{C}-\text{O}-\text{R}_3 \end{array}$
Carboxylic acid ester (northern regions)	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}_4-\text{C}-\text{O}-\text{R}_5 \end{array}$
Carboxylic acid amide	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}_6-\text{C}-\text{N}-\text{R}_8 \\ \\ \text{R}_7 \end{array}$

Model sulphur compounds

Sulphur compounds, which are present in a considerable amount in unhydrotreated diesel fuel, could have an impact on the lubricating properties of the base fuel. In order to assess this, we needed to select the sulphur compounds that are the main components present in diesel fuel. Sulphides, disulphides, mercaptans, alkylated derivatives of thiophene, benzothiophene and dibenzothiophene, are the main types of sulphur compounds that occur in gas oil [14]. In low sulphur diesel dibenzothiophene (DBT), benzothiophene (BT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) (Table 2) are the main sulphur compounds present because they are the most difficult to remove by hydrodesulphurization [15,16]. These compounds are therefore the only sulphur compounds that can contribute to the difference in lubricity between ULSD and low sulphur diesel. These were the components selected for our investigation.

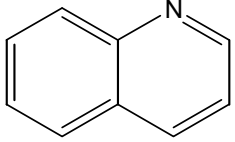
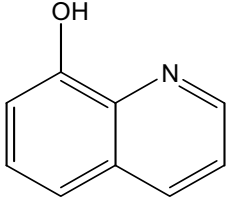
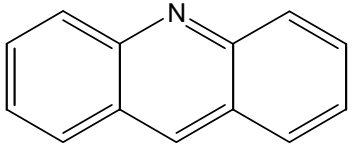
Table 2: Sulphur compounds [16]

benzothiophene	
dibenzothiophene	
4,6-dimethyl-dibenzothiophene	

Model nitrogen compounds

Beside sulphur compounds, other polar compounds like nitrogen-containing compounds - found in untreated gas oil and removed by HDS - may affect lubricity [16]. Typical nitrogen compounds which can be found in crude oil fractions comprise derivatives of aniline, pyrrole, pyridine, quinoline, acridine, indole and carbazole [15-19]. It has been demonstrated that pyridine, pyrrole, quinoline and indole showed a wear decrease pattern at 10000 ppm in a hydrotreated diesel fuel in a pre-version of the HFRR (among others differences fuel temperature 20 °C, stroke length 0.5 mm) from wear scar diameters of 0.35 mm (base fuel) down to values between 0.15 mm and 0.22 mm [20]. For 8-hydroxyquinoline, this effect could also be seen at a nitrogen content of 100 ppm. It was also observed that oxygen-containing derivatives of heterocyclic nitrogen-containing compounds have superior antiwear properties to the corresponding nitrogen compound [21]. The nitrogen compounds used in this work are displayed in Table 3. The nitrogen contents of the gas oils used in this work range from 15 ppm to 164 ppm before HDS (Table 5, Figure 6). Therefore, the impacts of quinoline and 8-hydroxyquinoline have been assessed at a similar nitrogen content of 20 ppm and 100 ppm. This is a factor from 500 and 100 times lower than what was investigated in the work by Wei [20]. The possible effect of acridine, another possible nitrogen-containing compound, has not been investigated in previous work, yet. Therefore, we also added this substance in our investigation.

Table 3: Nitrogen compounds [16]

quinoline	
8-hydroxyquinoline	
acridine	

2.2 TRIBOLOGICAL TEST METHODS

For the tribological characterisations of diesel fuels and lubricity additives two different test rigs were used. The HFRR test method is the standard technique for the assessment of diesel fuel lubricity and has been used to obtain a lubricity profile of all the fuels/additives tested in this study. A second test rig, the High-Temperature Oscillating Machine (HiTOM), has been the main test apparatus selected because it allows to investigate different tribological conditions. This test also allows the use of different wear specimen geometries and higher and variable loads. The highly-stressed contact is intended to represent highly-loaded contacts present in FIEs.

High-Frequency Reciprocating Rig (HFRR)

The HFRR test method for diesel fuel lubricity according to ISO 12156 [22] is used for standard lubricity assessments in our study. A detailed setup of the test rig and standard test parameters according to ISO 12156 can be found in the appendix (Figure 18). All tests were performed two times with the average corrected wear scar diameter (WS1.4) used in all the figures presented. For tests with varying fuel temperatures, WS1.4 is not defined so the mean wear scar diameter (MWSD) is used. Error bars represent the minimum and maximum values of the experiments. It has been shown that experiments with this test rig can also be assessed by measuring the wear volume of both specimens to get even more information from an HFRR test [23].

High-Temperature Oscillating Machine (HiTOM)

The test rig (Figure 1) HiTOM (High-Temperature Oscillating Machine) has been designed by BOSCH to reproduce in a controlled environment the main contacts that are present in the drive of Common Rail pumps. The machine kinetics of the chosen machine element are tribological similar to the real conditions experienced in

the high-pressure pump. The rig consists of a test chamber where the test specimens are immersed in diesel fuel that can be controlled to a temperature range from ambient to 90 °C. In the chamber a cylinder wear specimen is sliding in a reversing motion on a plate wear specimen. The oscillating motion is driven by an electric motor and a crankshaft with a frequency of 5 Hz and a stroke length of 10 mm. The normal force F_N (load) of up to 10000 N is applied to the tribological contact by a hydraulic cylinder. The resulting friction force F_F is measured at the lower wear specimen via a piezoelectric force gauge. Photographs of the test rig and the chamber are displayed in the appendix (Figure 19).

The cylinder specimen, which is an original part of a Common Rail pump, is made of annealed tool steel AISI M2. The plate as counter body which represents the raceway of a pump camshaft is made of the same annealed bearing steel AISI E-52100 as the original component with an equivalent heat treatment and surface finish. These materials are the latest used in Common Rail systems and are very likely to be the choice also for future FIE. Further details on the specimen can be found in Table 4. This test method is not standardized and is not intended to substitute the HFRR standard technique. The advantage of this technique is that it can provide information about the load-carrying capacity of different fuel compositions in highly-stressed contact environments that can be found in a real system. The load-carrying capacity has a direct link to the limit of performance of the fluid tested. In order to detect the transition from mild wear to incipient scuffing a series of tests has to be performed [24]. Each single test runs for 10 minutes at a fixed load with a fuel bath temperature of 60 °C. This results in a mean sliding velocity of 0.1 m/s.

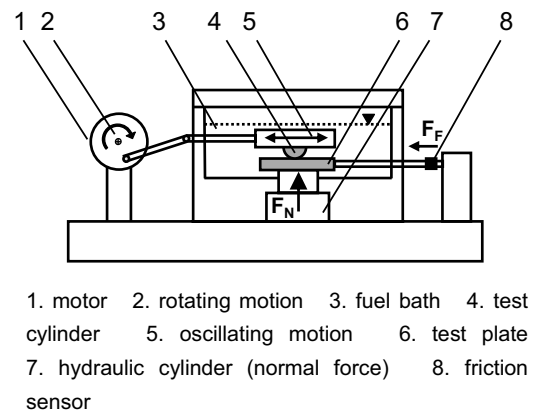


Figure 1: Setup of HiTOM test rig

Table 4: HiTOM test parameters

Parameter	Value
Test parameters	
Normal force	1000...10000 N
Stroke length	10 mm
Oscillating frequency	5 Hz
Fuel temperature	60 ± 2 °C
Fuel volume	4500 ml
Test duration	10 min
Wear specimen	
Cylinder diameter	10 mm
Cylinder length	21.5 mm
Cylinder material	AISI M2
Cylinder hardness	850 ± 70 HV10
Cylinder roughness	$R_a < 0.03$ μm
Plate material	AISI E-52100
Plate hardness	748 ± 19 HV10
Plate roughness	$R_a < 0.1$ μm
Ambient conditions	
Temperature	24 ± 2 °C
Relative humidity	50 ± 5 %
Hertzian pressure	400...1790 N/mm ²

Each test is performed twice to define a more representative value of the load-carrying capacity of the fluid under investigation. To find the transition from the mild wear regime to the scuffing regime, the wear scars of all tests are compared. A characteristic feature of incipient scuffing is the significant widening of the wear scar on the cylinder and the formation of shining bands on the plate. At a load of 1000 N the wear scar on the cylinder features a constant width of about 400 μm across the whole length of the line contact. At 1500 N and 2000 N the wear scar is significantly wider (600 μm to 700 μm) with signs of incipient scuffing which indicates that more severe wear is occurring (Figure 2).

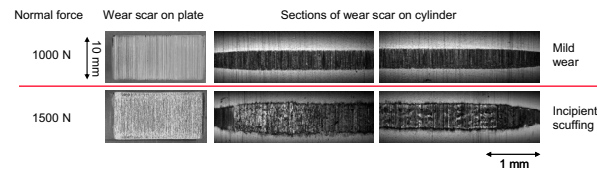


Figure 2: Wear scars on plate and cylinder at varying loads (ULSD 1; 60 °C, 5 Hz)

As a quantitative criterion for the transition from mild wear to incipient scuffing, the maximum wear scar width (WSW_{max}), the location with the widest extension of the wear scar on the cylinder, is measured with a microscope (Figure 3). The WSW_{max} values of all tests in

one series of tests for the same fuel are plotted versus the normal force (Figure 4). The load-carrying capacity for a certain fluid can then be drawn from this plot where values for WSW_{max} begin to exceed the constant level seen in experiments with lower loads. The incipient scuffing load determined in this work is the load at which at least one of the two tests measures widening of the wear scar with the constraint that no experiment at a lower load results in incipient scuffing. The load is increased from one test to the next by 1000 N. If the next higher load leads to incipient scuffing the next test will be performed 500 N below that load. This way the load interval from the last test with both “pass-runs” to the first test with incipient scuffing is reduced to 500 N. The error bars in all the HiTOM experiments represent this interval between “last pass” and “first failure”. The terms incipient scuffing load and load-carrying capacity are used with an equivalent meaning. The measurement of the widest wear scar extension instead of the average wear scar width can only provide the necessary information of incipient scuffing. Experiments demonstrate that incipient scuffing is rather a local effect and is not always occurring across the whole length of the contact. Sometimes experiments above the critical load do not show incipient scuffing. This can be explained by the fact that this is an incipient effect which is affected by slight variations of specimen material and fuel composition. FIE needs protection against the failure mechanism of incipient scuffing because this may reduce performance and lifetime.

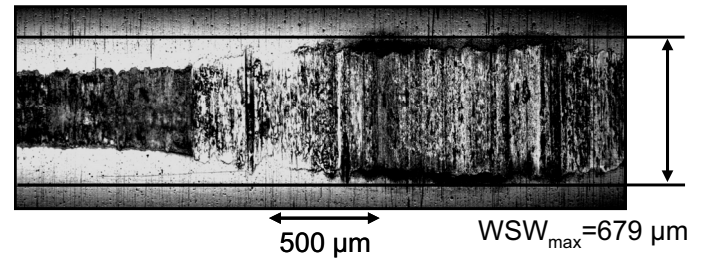


Figure 3: Measuring of maximum wear scar width WSW_{max}

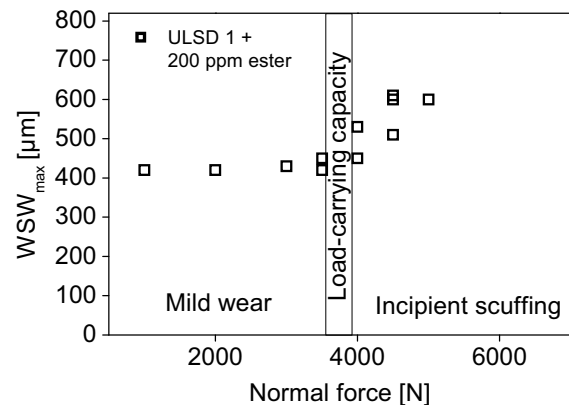


Figure 4: Plot of a test series to find one LCC

The surfaces of HiTOM wear specimens that have exceeded their load-carrying capacity (LCC) are characterised by signs of incipient scuffing. On both specimens the wear scars show a higher surface roughness than the specimen that were tested below their LCC which have very smooth surfaces. The cylinder features a transition to higher wear, expressed in WSW_{max} . Material from the cylinder is transferred to the plate, as can be seen from further analyses. This becomes obvious from the different appearance of the plate showing metallic shining bands along the sliding direction at locations of wear scar widening on the cylinder.

3. RESULTS AND DISCUSSION

3.1 IMPACT OF FUEL COMPOSITION

Impact of base fuel

The base fuels without any additive content have been tested in HFRR and HiTOM. The lubricity values range from 699 μm for the Class I to 236 μm for the fuel with 5 % RME content (Figure 5). Apart from the fuel that is blended with 5 % biodiesel and has an excellent lubricity, ULSD 1, ULSD 2 and Class I have a lubricity level that does not meet the EN 590 European diesel fuel specification [25]. According to [26] and [27] the good lubricity with $WS1.4 < 460 \mu\text{m}$ of biodiesel is caused by the presence of free carboxylic acids and mono-acylglycerol contaminants because of their oxygen-containing polar moieties.

The assessment of the incipient scuffing load with the HiTOM test of the base fuels indicates that, like for the HFRR test, there is a wide range of LCC from 1250 N for the Class I and ULSD 1 to 4750 N for the 5 % RME diesel (Figure 5).

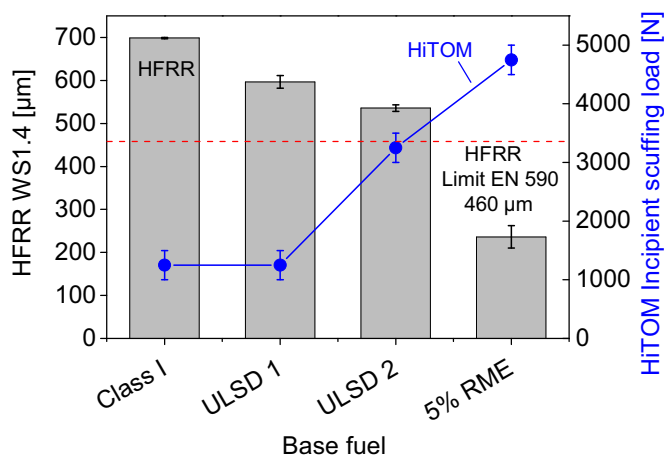


Figure 5: Lubricity and scuffing load of different base fuels

Impact of hydrodesulphurization (HDS)

Deep-desulphurization of diesel fuels leads to field failures of FIE when the fuel is not additive-treated [1,2]. Although it is obvious that HDS is responsible for the

decrease of lubricity, there has not yet been any direct comparison of the lubricity of gas oil right before and right after HDS. The comparisons of HFRR lubricity measurements of the gas oil samples, light gas oil (LGO), medium gas oil (MGO) and gas oil (GO) before and after HDS are displayed in Figure 6. The sulphur-containing gas oil samples have a lubricity value $WS1.4$ between 400 μm and 500 μm before HDS. After the HDS, the virtually sulphur-free gas oil samples have a poor lubricity performance with values between 550 μm and 650 μm . These experiments clearly demonstrate that HDS is the process which is responsible for the decrease of lubricity. During hydrotreatment in order to reduce the sulphur content the nitrogen content is reduced as well. The hydrodesulphurization process removes hetero-compounds (containing nitrogen, oxygen, sulphur) which are able to adsorb on metal surfaces and protect the sliding bodies.

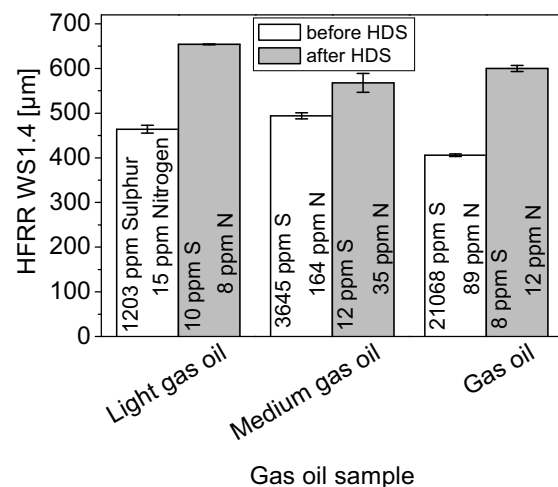


Figure 6: Lubricity of gas oil samples before and after hydrodesulphurization

The impact of HDS on the load-carrying capacity in the HiTOM was investigated with the light gas oil sample since this sample was available in the right amount and LGO showed a stronger lubricity decrease in the HFRR than MGO. During the hydrotreatment process the LCC is significantly decreased from 3250 N down to 1750 N (Figure 7). To summarize the experiments with both test methods, HDS impacts both lubricating properties, lubricity (according to HFRR) and load-carrying capacity.

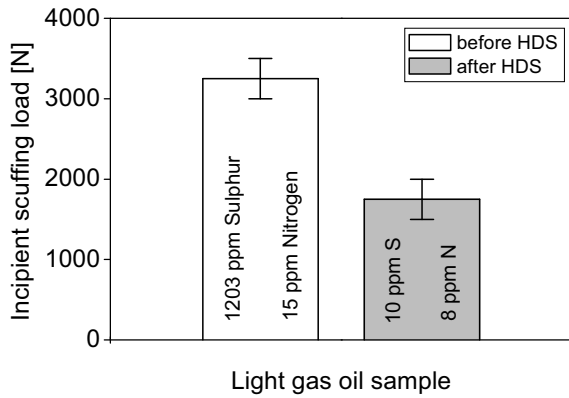


Figure 7: Load-carrying capacity of light gas oil before and after HDS

Impact of sulphur and nitrogen compounds

As can clearly be seen from the results of the previous experiments, the hydrodesulphurization process drastically reduces the lubricity and the LCC as well as reducing the sulphur content of the light gas oil from 1203 ppm to 10 ppm and the nitrogen content from 15 ppm to 8 ppm (Table 5). To answer the question whether the inherent lubricity of untreated gas oil was lost by the decrease of sulphur and nitrogen compounds these type of compounds were added back into fuel.

Undoubtedly, the intention of this work is not to propose the addition of sulphur and nitrogen compounds as lubricity improvers, but instead to further understand how changes in diesel fuel composition had impacted the inherent lubricity of diesel fuel.

In the HFRR the sulphur compounds dibenzothiophene (DBT), benzothiophene (BT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) were added to ULSD 1 to achieve a sulphur content of 1000 ppm because this level is similar to the sulphur content of the LGO before HDS. For the case of DBT the sulphur content was also raised to 5000 ppm.

The addition of the three compounds to ULSD 1 shows no significant effect on the improvement of the base fuel lubricity (Figure 8).

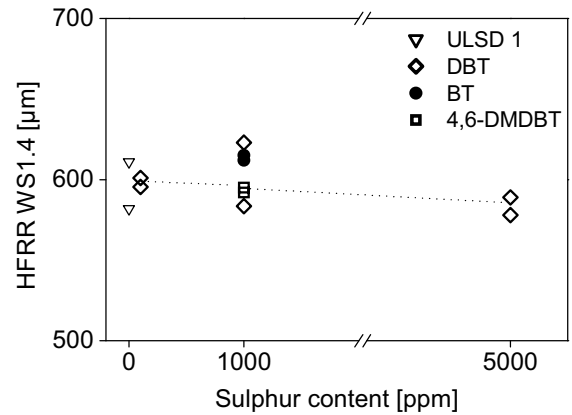


Figure 8: Impact of sulphur compounds on lubricity

Sulphurized compounds, especially long-chain sulphides and disulphides are well known as so-called extreme-pressure additives [28-30] which can prevent scuffing and seizure of highly-loaded contacts. For DBT, which is not a sulphide, this has not been demonstrated yet. For investigations with the HiTOM only DBT was selected. The impact of this compound has been investigated at a sulphur content of 1000 ppm in ULSD 1. These experiments demonstrate an increase of LCC by 1000 N by the addition of DBT (Figure 9). The protecting mechanism is the formation of complex layers of ferrous sulphide [31]. Contact conditions in the HFRR may not be severe enough to enable the reaction and subsequent formation of these layers.

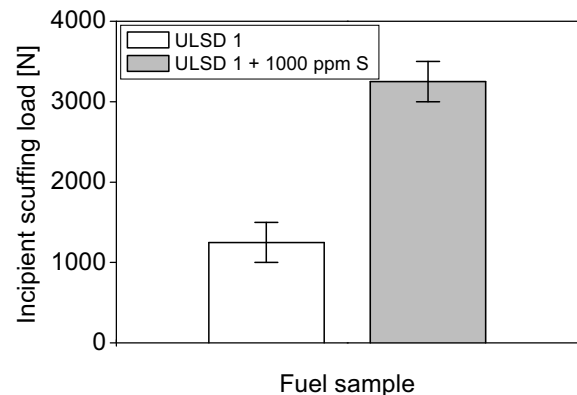


Figure 9: Impact of sulphur as DBT in ULSD 1 on incipient scuffing load

As can be concluded from these experiments, sulphur compounds in untreated diesel fuel are not providing lubricity protection, although DBT can give a benefit in the HiTOM. This is consistent with previous work [20]. The reason for base fuel lubricity has been investigated and many authors have claimed that polar oxygen-containing and polyaromatic compounds act as

boundary lubricants and thus are responsible for lubricity [8,20]. Other authors stated that the low aromatics content of low and ultra-low sulphur diesel fuels is the reason for the lack of lubricity [32]. During HDS the nitrogen content of the gas oil samples is reduced as well as the sulphur content (Table 5; Figure 6). It has been demonstrated that the nitrogen compounds pyridine, pyrrole, quinoline, indole can significantly reduce the wear scar diameter of a hydrotreated diesel fuel at a nitrogen content of 10000 ppm [20]. In this work the impact on lubricity of acridine, quinoline and 8-hydroxyquinoline (Table 3) was evaluated. The compounds were added to ULSD 1 at nitrogen contents of 20 ppm and 100 ppm. These contents are similar to concentrations found in our gas oil samples before HDS (Table 5, Figure 6).

Acridine and quinoline provide some improvement of lubricity at a nitrogen content of 100 ppm from 597 μm to 542 μm and 555 μm respectively (Figure 10). At a nitrogen content of 20 ppm there is no significant decrease of WS1.4. 8-hydroxyquinoline shows a very strong reduction of the wear scar diameter at a nitrogen concentration of 20 ppm from 597 μm to 269 μm and an excellent lubricity improvement at 100 ppm to WS1.4 of 160 μm . Although 8-hydroxyquinoline has a chemical structure similar to quinoline and acridine the aromatic ring of the former structure is substituted by a hydroxyl-group. According to [21] the hydroxyl-group with its polarity enhances the adsorption of this molecule at the surfaces of wear specimens. These results demonstrate that the huge variety of aromatic nitrogen compounds with the enormous diversity of its derivatives does account for lubricity of untreated base fuels.

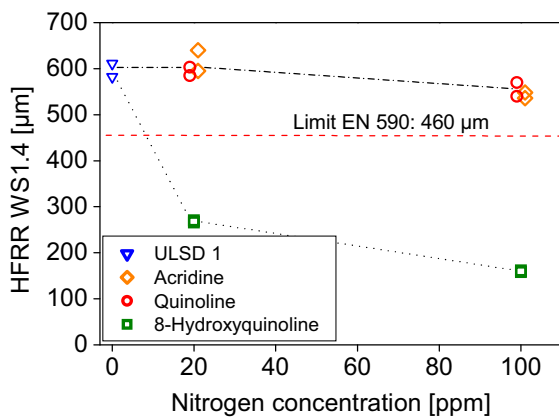


Figure 10: Impact of nitrogen compounds on lubricity

3.2 COMMERCIAL LUBRICITY ADDITIVES

Impact of commercial lubricity additives on lubricity - HFRR

The four commercial additives tested can deliver good lubricity improvement at a treat rate of 200 ppm in a variety of base fuels (Figure 11) to a level below the European requirement of 460 μm maximum [25]. Even for the fuel which contains 5 % RME and exhibits a good lubricity of 236 μm without any additive content, its lubricity can be improved to some extent (about 40 μm) by the addition of lubricity additives.

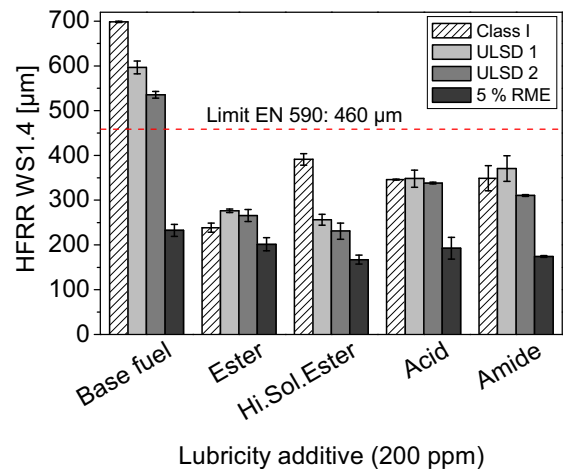


Figure 11: Impact of lubricity additives (200 ppm) on lubricity of different base fuels

The effect of an increasing additive concentration in base fuel ULSD 1 between 0 ppm and 2000 ppm on the HFRR lubricity can be seen in Figure 12. Between 0 ppm and 200 ppm the WS1.4 responds significantly to the increasing additive content. At 1000 ppm there is some further lubricity improvement which can be extended by less than 50 μm at 2000 ppm. Although all four chemistries show a levelling of performance at high concentrations (>1000 ppm) there is a significant difference between the additives tested. Both esters can reach WS1.4 of about 160 μm . The acid and the amide, on the other hand, can only reach lubricity levels of 260 μm and 300 μm respectively (Figure 12). These data clearly indicate that higher treat rates can achieve further lubricity improvement.

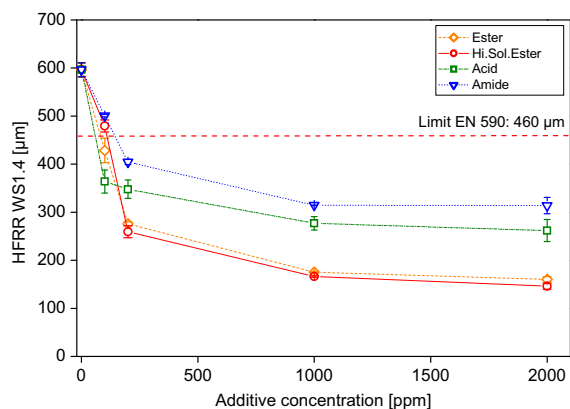


Figure 12: Response of lubricity to increased additive concentration

Impact of commercial lubricity additives on load-carrying capacity - HiTOM

The impact of the four different lubricity additives on the tribological behaviour in the HiTOM was tested at 200 ppm in base fuel ULSD 1. All compounds give a strong increase of the incipient scuffing load, from 3750 N to 4750 N in a fuel that has a base untreated value of 1250 N (Figure 13). The high solubility ester performs significantly better than the other additives.

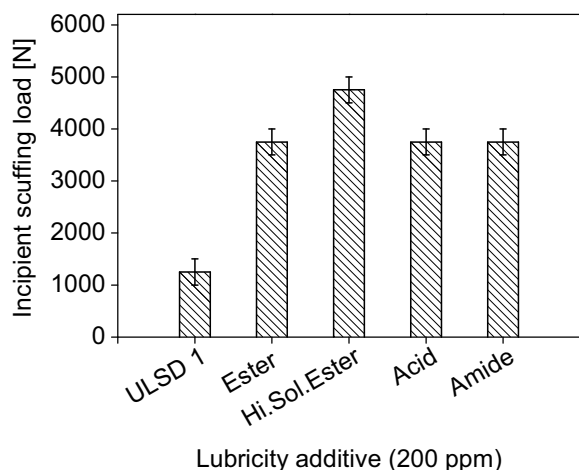


Figure 13: Impact of lubricity additives (200 ppm) in ULSD 1 on incipient scuffing load

Future applications - due to increased injection pressure requirements or transient conditions in current applications due to sliding conditions - could require further protection to ensure that the fuel injection system retains its integrity. Therefore, the ability of the different lubricity additives to extend the LCC has been evaluated also at higher treat rate, 1000 ppm. Most of the work focuses on ester- and acid-based lubricity additives because they are more widely used in market than the other additive chemistry.

With an increasing concentration there is an increase of LCC (Figure 14). The acid can provide a minor increase of 500 N to 4250 N, whereas the ester-based lubricity additive can provide an increase of 2000 N, reaching an LCC value of 5750 N. This significant difference can be attributed to differences of their molecular structure and their ability to form a more resistant adsorption layer on the metallic surfaces.

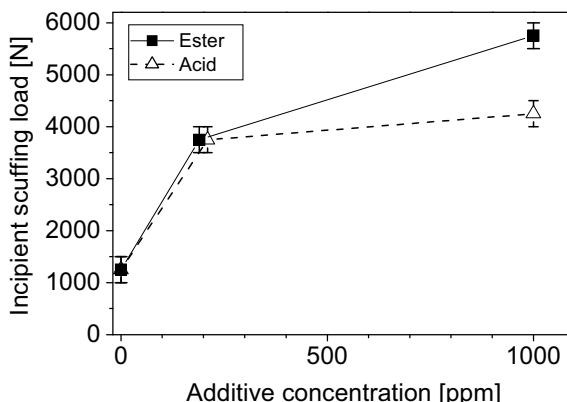


Figure 14: Impact of increased additive treat rate in ULSD 1 on incipient scuffing load

3.3 VARIATION OF TEST TEMPERATURE

As mentioned in the previous chapter, current and future FIE systems could experience more severe operating conditions that may pose additional thermal stress on the tribological contacts. For this reason, HFRR tests have been performed at higher temperatures than 60 °C to investigate whether current lubricity additives can also provide protection at higher temperature.

HFRR tests have been performed between 30 °C and 149 °C (HFRR limit). For tests run at temperatures different from 60 °C, the calculation of the corrected wear scar diameter WS1.4 is not defined. Therefore, the measurement used is the mean wear scar diameter (MWSD) without humidity correction.

Between 30 °C and 120 °C the MWSD of the base fuel and the base fuel with a content of 100 ppm of an antioxidant additive increases from about 560 µm to about 620 µm (Figure 15). A typical fuel antioxidant additive was added to prevent any oxidation process. The comparison between the two sets of results, without and with antioxidant, allowed us to further understand the value of the results obtained and possibly decouple the true lubrication process from that provided by degradation products.

For the fuel containing 200 ppm of the ester additive the MWSD increased from 215 µm to 380 µm between 30 °C and 120 °C. For the fuel containing 200 ppm of the acid additive the MWSD is increasing from 196 µm at 30 °C to 388 µm at 90 °C. This effect may be caused by a

variety of mechanisms like decreasing film strength of the additive adsorption layer and a change in the additive adsorption/desorption rate. Whatever the mechanism is, an increase in fuel temperature leads to an increase in wear rate.

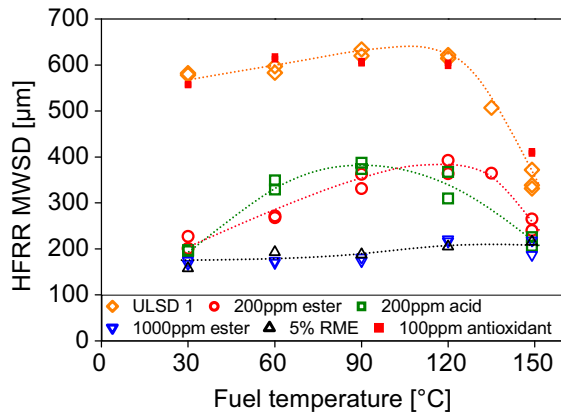


Figure 15: Impact of fuel temperature on mean wear scar diameter on ball specimen

The MWSDs of the fuel containing 5 % RME and ULSD 1 containing 1000 ppm of the ester are not significantly varying over the whole temperature range between 30 °C and 149 °C. The concentration of 1000 ppm of ester additive is high enough to compensate the effects of an increasing desorption rate at increasing temperature. Above 120 °C the MWSD is also decreasing for the base fuel ULSD 1 down to 350 µm. The same pattern can be seen with the fuel containing 200 ppm ester or 100 ppm antioxidant. For the acid additive this decrease begins between 90 °C and 120 °C. However, the minor difference in temperature is unlikely to be significant and indicate a different behaviour for this chemistry. However, with increasing temperature, there is an increasing loss of fuel. At test temperatures of 149 °C about 75 % of the fuel was evaporated from the fuel reservoir by the end of test, - after 75 minutes - leaving a sticky viscous liquid in the fuel bath. Further investigation was carried out in order to understand the impact that the fuel loss has on the test results. In order to do this, the test fuel ULSD 1 was also stripped in a beaker so that about 75 % of the initial volume had evaporated within 75 minutes at 149 ± 5 °C. This hopefully simulates what happens during the HFRR test at high fuel temperature. Then, the fuel was analysed. These samples had a total acid number forty times that of the base fuel and the viscosity had increased by factor 2.3. This experiment at 149 °C clearly demonstrates that the base fuel properties are strongly affected by oxidation and evaporation. At the same time, it also indicates that this type of condition, if experienced for long in the tribological contacts may degrade the performance of the fuel injection system. For the purpose of our study, trying to understand the behaviour and potential of additives, our investigation was limited to a maximum temperature of 120 °C because above this value mechanisms like accelerated fuel evaporation and thickening, fuel degradation by

oxidation are involved. Therefore, any additive impact can not clearly be decoupled and measured. Apart from the test with a standard temperature of 60 °C in the HiTOM, experiments were also performed at a bulk temperature of 90 °C. In order to exclude the effect of fuel ageing, 100 ppm of a typical fuel antioxidant additive was added. During each test series fuel samples were taken from the bath for the evaluation of the total acid number. All the results indicated that the acid content, caused by fuel ageing, was not increasing during a series of experiments. Therefore, it is very likely that this side effect can be completely ruled out. The load-carrying capacity of the additive-treated fuel is not decreased at 90 °C (Figure 16) and the protection of the tribological contact against incipient scuffing is retained. The base fuel has a significantly higher LCC at 90 °C than at 60 °C. This is in contrast to the HFRR results where an increasing temperature between 30 °C to 90 °C/120 °C increases the wear with both base fuel and additive treated fuel. Moreover, the results with the HFRR confirm that both lubricity additives provide lubricity benefits over the temperature range tested. Experiments with the HiTOM indicate that the ester-based additive can provide a benefit for the LCC at 60 °C and 90 °C.

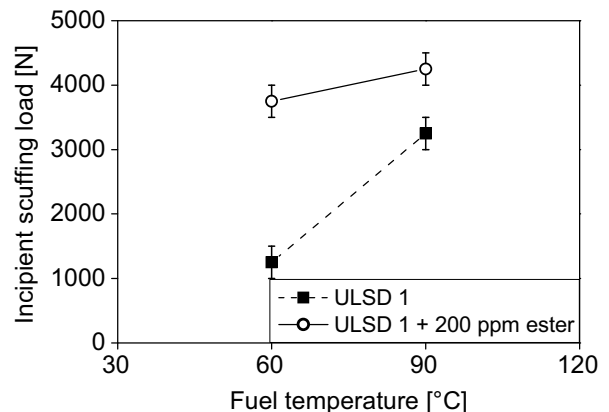


Figure 16: Impact of variation of fuel temperature on incipient scuffing load

3.4 CORRELATION OF HITOM AND HFRR RESULTS

The experiments carried out in previous sections can be used to see whether there is a correlation between the two tests, the HFRR and the HiTOM. The results generated on fuels untreated and treated with additives show an excellent correlation between both tests methods (Figure 17). Fuel samples with a poor lubricity in the HFRR ($WS_{1.4} > 460$ µm) also have a low load-carrying capacity in the HiTOM ($LCC < 3000$ N). Additive-treated fuels, as expected, give HFRR results and this is mirrored by their relatively high (> 3000 N) load-carrying capacity.

When HFRR values are very low, indicating excellent lubrication ability, this is again reproduced in the HiTOM environment generating contact loads greater than 4000 N. Therefore, it would seem possible to extend the use of the HFRR, a method, which is common in the industry, to the more highly loaded contacts that could be seen in the future with more advanced fuel injection systems. However, this protection can only be achieved if the fuel HFRR value is substantially lower than that required by current fuel specifications.

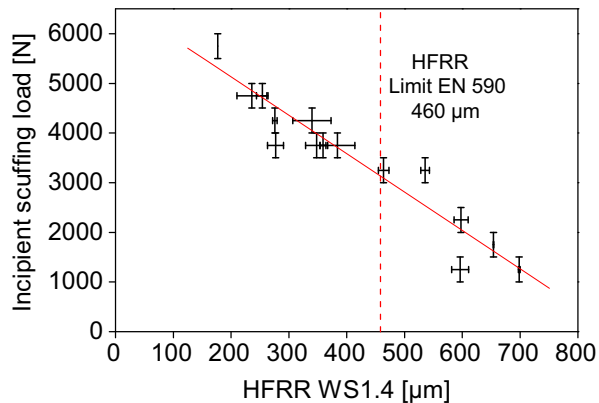


Figure 17: Correlation of incipient scuffing load and lubricity

CONCLUSION

The objective of the work carried out was to increase the knowledge of the tribological behaviour of different fuel compositions in a highly-loaded contact that are likely to appear in future fuel injection applications. The data developed can provide information on the performance of current fuels and different lubricity additive technologies under more severe tribological conditions. The main conclusions of our work are:

1. The lubrication ability of diesel fuels, measured using the HFRR lubricity and with the critical load of incipient scuffing (load-carrying capacity) in the High-Temperature Oscillating Machine (HiTOM) is dependent on the composition of the base fuels and the treat rate and type of lubricity additives used. A content of 5 % RME in fuel increases the load-carrying capacity and decreases the lubricity value WS1.4.
2. Hydrodesulphurization decreases the lubricity reserve of gas oil by 80 -200 µm (HFRR) and the load-carrying capacity by 1500 N in the HiTOM. Model sulphur compounds do not restore the lubricity of a hydrotreated diesel fuel. However, dibenzothiophene can increase the load-carrying capacity. Therefore, the removal of sulphurised compounds is not the major reason for the loss of lubrication of ultra low sulphur diesel fuels

3. The model nitrogen compound 8-hydroxyquinoline improves the lubricity at very low concentrations (20 ppm nitrogen) whereas quinoline and acridine need a higher concentration (100 ppm nitrogen) for some lubricity improvement. This indicates that the removal of nitrogen containing compounds is likely to result in a diesel fuel with poorer lubricity performance.
4. Different lubricity additive technologies with carboxylic acid-, ester- and amide based chemistries can increase the lubricity in a variety of base fuels at a concentration of 200 ppm to meet the lubricity requirement according to EN 590. These compounds can also provide protection against adhesive wear by increasing the incipient scuffing load.
5. Higher than market-typical additive concentrations can further increase lubricity but are levelling at concentrations between 1000 ppm and 2000 ppm. The ester-based additives level at a better value than the acid- and amide based additives and so can provide more protection to FIE.
6. The load-carrying capacity of ULSD 1 can be increased by 4500 N by an ester based lubricity additive treat rate of 1000 ppm. The acid based additive can only provide an increase of 2500 N at 1000 ppm treat rate..
7. The ester-based additive (200 ppm) can provide an improvement of the load-carrying capacity by 3000 N at a fuel temperature of 90 °C.
8. There is a good correlation between the HiTOM test, that uses real components of a Common Rail pump as test samples, and the HFRR. This suggests that the HFRR could successfully be used should the extra lubricity protection be required in the market place.

It is imperative that current and future FIE operate without any problem in use to ensure that vehicles perform as required. The study completed confirms that this can be achieved even for tribological conditions that well exceed today's requirements.

ACKNOWLEDGMENTS

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APPENDIX

Table 5: Properties of base fuels

Property	Unit	Base fuels				Requirement EN 590	Test method
		Swedish Class I	ULSD 1	5 % RME	ULSD 2		
Comment	-						
Sulphur content	mg/kg	3	2	10	31	10	EA ¹⁾
Nitrogen content	mg/kg	2	2	45	3	not spec.	EA ¹⁾
Water content	mg/kg	10	30	130	31	200	EN ISO 12937
Density at 15 °C	kg/m ³	811	823	836	831	820...845	EN ISO 3104
Viscosity at 40 °C	mm ² /s	1.9	2.8	2.4	3.2	2.0...4.5	EN ISO 3104
Distillation						-	
% (V/V) recovered at 250 °C	% (V/V)	70	25	42	24	< 65	EN ISO 3405
% (V/V) recovered at 350 °C	% (V/V)	> 95	> 95	> 97	98	> 85	
95 % (V/V) recovered at	°C	278	315	335	332	< 360	
Fatty acid methyl ester (FAME) content	% (V/V)	0	0	5	0	0...5	EN 14078

¹⁾ Elemental Analyzer ANTEK 9000

Table 6: Properties of gas oils

Property	Unit	Gas oil samples						Requirement EN 590	Test method
		Light Gas Oil (HDS feed)	LGO hydrode-sulphur-ized	Medium Gas Oil (HDS feed)	MGO hydrode-sulphur-ized	Gas Oil (HDS feed)	GO hydrode-sulphur-ized		
Comment	-								
Sulphur content	mg/kg	1203	10	3645	12	2168	8	10	EA ¹⁾
Nitrogen content	mg/kg	15	8	164	35	89	12	not spec.	EA ¹⁾
Water content	mg/kg	134	63	94	37	103	22	200	EN ISO 12937
Density at 15 °C	kg/m ³	811	811	853	846	829	849	820...845	EN ISO 3104
Viscosity at 40 °C	mm ² /s	1.6	1.6	3.3	3.3	2.8	2.8	2.0...4.5	EN ISO 3104
Distillation								-	
5 % (V/V) recovered at	°C	175	180	200	205	211	211	not spec.	EN ISO 3405
% (V/V) recovered at 350 °C	% (V/V)	> 95	> 95	n/a	n/a	n/a	n/a	> 85	
95 % (V/V) recovered at	°C	300	300	365	360	358	358	< 360	

¹⁾ Elemental Analyzer ANTEK 9000

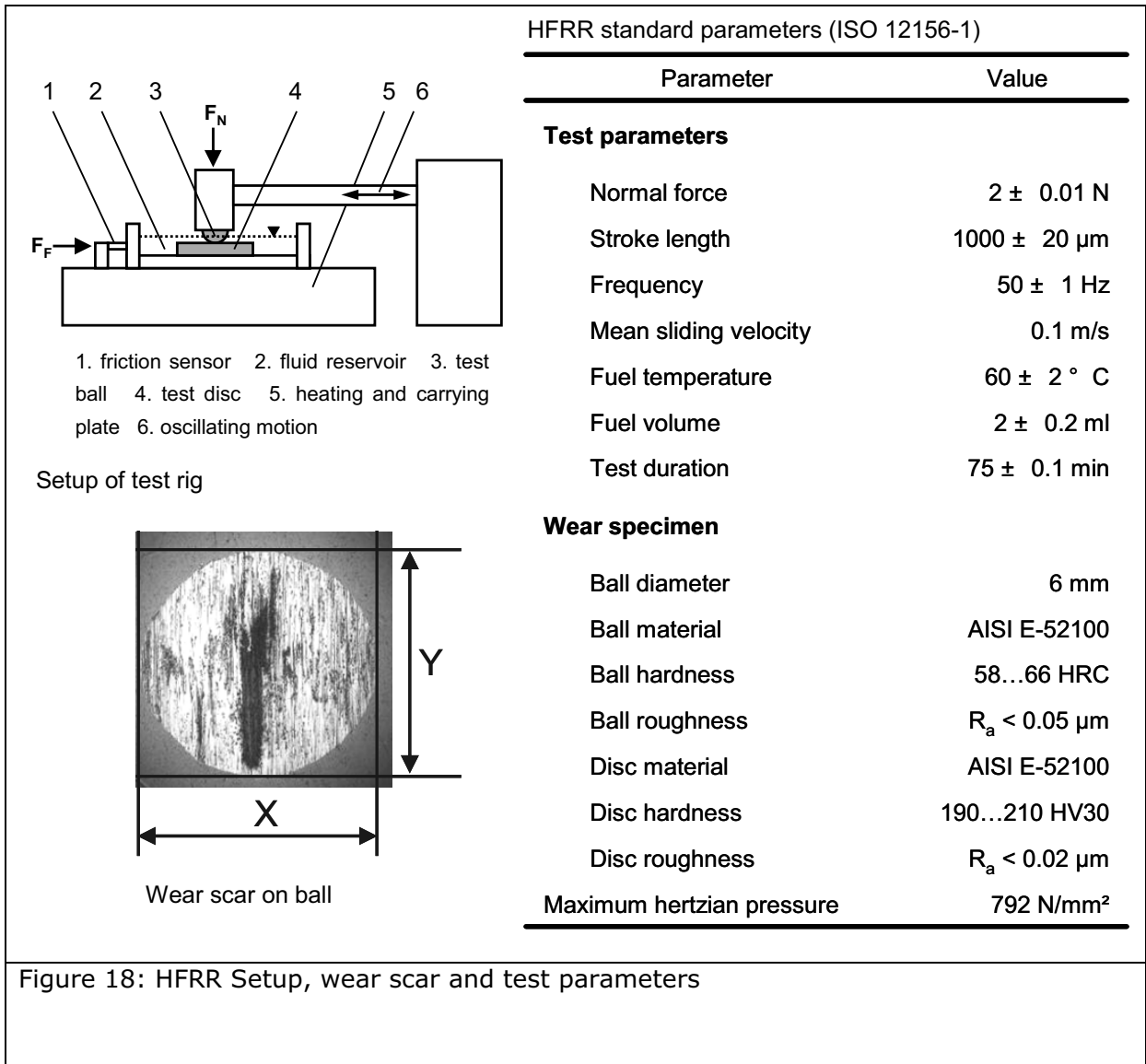


Figure 18: HFRR Setup, wear scar and test parameters

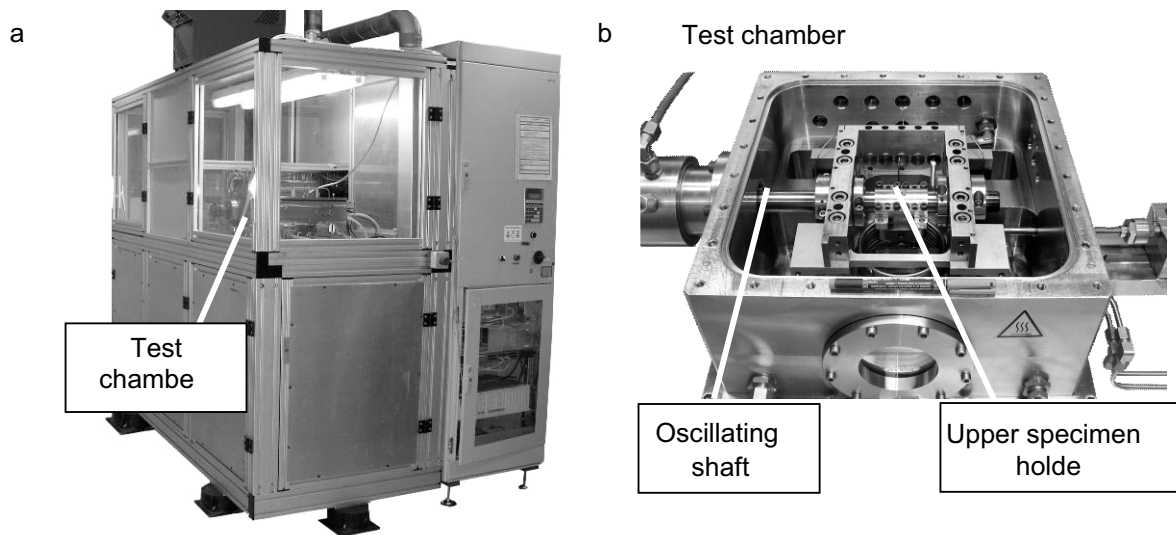


Figure 19: a) Overview of High-Temperature Oscillating Machine (HiTOM),
 b) Test chamber (370 mm x 370 mm x 180 mm)