Original Article

Institution of MECHANICAL ENGINEERS

Journal of ENGINEERING TRIBOLOGY

Proc IMechE Part J:
J Engineering Tribology
1–14

Article reuse guidelines:
sagepub.com/journals-permissions
DOI: 10.1177/13506501251351790
journals.sagepub.com/home/pij
Sage

The effect of combustion on MoDTC friction reduction capabilities determined by engine tests

Abdullah Nashmi Alenezi[1], Cayetano Espejo[1], Quentin Arnoux[2], Catherine Charrin[2], Benoît Thiébaut[2] and Ardian Morina[1]

Abstract

Molybdenum Dithiocarbamate (MoDTC) is an excellent friction modifier used in oil formulations for internal combustion energies. In the search of minimising transition metals contents in lubricating oils, extensive work has been carried out in benchtop tribometers to produce optimised formulations. However, tribometers present major limitations mimicking the extreme environment present within the engine cylinders and assessing the effect of this environment on the tribochemistry of this additive. This work presents a combined analysis using single-cylinder engine tests and surface analysis techniques: Raman and XPS. Raman microscopy maps the distribution of MoS_2 and XPS identifies all the molybdenum species formed by tribochemistry. This approach enabled assessment of the effect of the combustion on MoDTC by comparing the results of experiments executed under fired and motored conditions. Areas where the MoS_2 solid lubricant and other molybdenum species formed were identified on the liner and linked to the corresponding friction force attained during the engine test cycle. As expected, the effective MoS_2 formation on returning points on the liner delivered efficient friction reduction. Noticeable differences in the tribochemistry of MoDTC and distribution of molybdenum species were found between fired and non-fired tests. In motored tests, MoS_2 was generated in both returning points, whereas in fired tests MoS_2 was generated only at the bottom, with oxidised molybdenum species present close to the top dead centre. Tribochemistry mechanisms under fired conditions are proposed. Understanding these mechanisms constitutes an invaluable tool to transfer the results obtained with bench tribometers to real engine operating conditions.

Keywords

IC engines, MoDTC, tribochemistry, Raman microscopy, XPS, floating liner tests

Date received: 20 February 2025; accepted: 5 June 2025

Introduction

In a context of limited energy resources and global warming it is paramount to find ways to reduce carbon dioxide emissions worldwide. Transportation currently accounts for 26% of the global energy demand, and internal combustion engines (ICEs) still play a critical role in the sector, with around 65 million of ICE passenger cars sold in 2022.[1] Despite the strong irruption of electric vehicles, and a forecast depicting a continuous sales decline in ICE cars, transition to a fully electric fleet will not take place within the timeframe required to take effective actions towards decarbonation.[2] In this scenario, actions aiming to reduce the reduction of fuel consumption and its associated carbon emissions will contribute to achieve the targets imposed by governments and supranational organisations.

Around 11.5% of the energy in a passenger car is used to overcome friction within the engine.[3] Reducing the friction within the engine has a direct effect on fuel economy, as not only the available energy is reduced, but also the energy that otherwise would be spent through the intrinsic thermal losses of the combustion cycle.

Frictional forces between the piston assembly and the cylinder in ICEs account for half of the engine friction energy losses. The complexity of the piston/cylinder system is manifested by all lubrication regimes (i.e., boundary, mixed, elastohydrodynamic…) co-existing at the piston ring/cylinder contact along each stroke.[4] At

[1]Institute of Functional Surfaces (IFS), School of Mechanical Engineering, University of Leeds, Leeds, UK
[2]Centre de recherche de Solaize, TotalEnergies OneTech, Chemin du Canal, France

Corresponding author:
Cayetano Espejo, Institute of Functional Surfaces (IFS), School of Mechanical Engineering, University of Leeds, Leeds, LS2 9JT, UK.
Email: c.espejoconesa@leeds.ac.uk

the reversal points (TDC and BDC), the boundary and mixed lubrication regimes dominate the contact while at the mid stroke, the hydrodynamic regime exists because of the high speed of the piston. It is worthwhile highlighting that at the reversal points, the film thickness is not zero due to the squeeze effect, but researchers have proved both numerically and experimentally that boundary friction peaks are produced on the proximity of the dead centres.[5,6] It is also well known that the power losses in this system mainly occur in the hydrodynamic regime (fluid shear losses), encouraging the use of reduced viscosity oils[7,8] to minimise overall friction energy losses. However, additional challenges arise from this measure. In particular, the range where boundary and mixed lubrication regime occur along the stroke is expanded, activating larger areas of asperity to asperity contact for longer, which would return higher friction and localised accelerated wear about the piston returning areas.[9]

A potential solution to alleviate localised boundary friction effect while keeping low viscosity oils for overall low friction performance is including in the oil formulations friction modifiers (FM). Amongst the most popular FM for ICE applications molybdenum dithiocarbamate (MoDTC) stands out as a highly efficient additive. The combination of MoDTC with low viscosity oils has already demonstrated a good performance in ICEs.[10,11]

Numerous studies depict the function of this additive by tribochemistry action.[12–19] Using benchtop tribometers and model lubricants, Khaemba et al. proposed a tribochemistry mechanism, consisting of physical shear stress activating MoDTC decomposition to generate amorphous molybdenum oxysulphide species. Later, under the presence of ferrous surfaces, sufficient mechanical stress and with the condition that a thermal threshold is overcome, these oxysulphides species will reduce to a fully crystalline MoS_2, a well-known solid lubricant that will reduce macroscopic friction by physical exfoliation of MoS_2 platelets in the nanoscale. This reaction pathway has clearly been identified under ideal testing conditions.[17] Similar findings in terms of the composition of the tribofilm were found by Al Kharboutly et al., confirming this reaction pathway using alternative characterisation techniques.[20] This tribochemistry reaction pathway also applies to trimmer organic molybdenum additives and even non-sulphur-containing organic molybdenum species can effectively develop a low friction tribofilm provided a suitable source of sulphur is added to the model oil, as proven by different research groups.[21–23]

When fully formulated motor oils are used instead of model lubricants, challenges arise in terms of the interactions promoting or restraining MoDTC effectiveness. The general consensus in the scientific community is that some sulphur-containing additives, such as the antiwear and antioxidant compound Zinc Dialkyl DithioPhosphate (ZDDP), play a synergistic effect with organic molybdenum compounds.[24–26] The interactions with other common additives, such as detergents, is less understood, but evidence shows that antagonistic effects prevent an effective MoS_2 formation.[27,28] Nevertheless, the presence of ZDDP seems to overcome such antagonistic effects, explaining why fully formulated motor oils exhibit friction reduction capabilities when MoDTC is blended, provided that boundary lubrication, adequate temperature and contact pressures are present in the tribological system.[29] Another key factor affecting MoDTC tribochemistry is the composition of the surfaces, which is especially relevant in engine where different materials and specialised coatings are used.[30–36]

Using appropriate surface mapping tools such as Raman microscopy, X-Ray Photoelectron Spectroscopy (XPS) and electron microscopy techniques, the MoS_2 distribution across and deep into the contact surface has provided valuable knowledge about how formation and distribution of MoS_2 can be linked to friction performance under ideal conditions,[29,37,38] and to some extent, explained how distribution and location of these MoS_2 deposits deliver friction reduction in piston-cylinder and engine systems.[39,40]

However, the low friction tribofilm formation mechanisms in the piston cylinder system within the engine, and the effect of the combustion on the MoDTC tribochemistry and its friction performance in a real scenario, are not fully understood. This motivates the use of single cylinder engine tests with *in-situ* friction measurement capabilities in combination with analytical techniques to facilitate a robust framework and enable the development of high-efficiency low viscosity oils.

Methods and materials

Engines

Floating liner

The cornerstone of this work is the use of a device with capabilities to provide instantaneous friction measurements between the piston and the cylinder as reciprocal piston movement occurs in this engine system. For this purpose, a 0.5 l AVL FRISC (FRIction Single Cylinder) floating liner concept, designed by AVL GmbH, was employed. The engine consists of a single cylinder supported by a series of sensors located between the cylinder and the crankcase, such the cylinder assembly "floats" over a fixed reference frame, as shown in Figure 1. The 0.5 litre displacement is given by a stroke of 92.4 mm and a diameter of 83 mm.

These series of four three-dimensional sensors acquire force information in the axial, lateral and longitudinal directions. The 12 different signals are processed to account for vibrations and crosstalk sensitivity to provide a well calibrated reliable friction force in the cylinder longitudinal direction (F_z). The acquired data is coupled with high accuracy measurements of the crankshaft angle (CA). Other key parameters were recorded, such as piston speed, water and oil temperature, pressure, etc. Further details on this rig operation can be found in.[41]

Experiments using this equipment were carried out in motored mode, i.e., a torque was applied on the crankshaft to maintain a certain speed, and in fired mode, where the engine was functioning by igniting a gasoline/air mixture

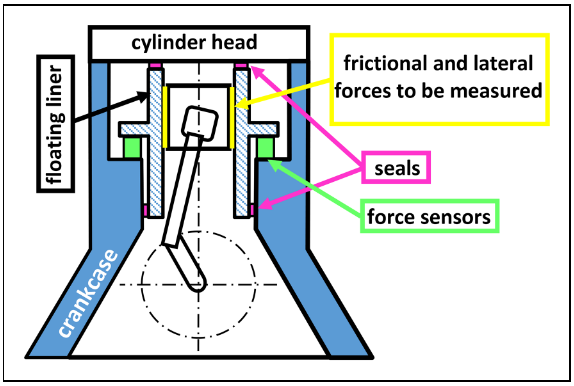

Figure 1. AVL FRISC floating liner concept. Adapted from.[41]

as in real working conditions. In both modes, a temperature of 90 °C was set for both the oil and the cooling water circuit in the engine. Ring packs consisted of a chromium-nitride coated 1st compression ring, a PVD-phosphate coated 2nd ring and an oil distribution ring also coated with chromium-nitride. Cylinder liners were made of EN-GJL-250 grey cast iron. After the installation, the system was cleaned with an oil containing detergents, and flushed twice. Once the cleaning procedure was complete, the system was run using the appropriate testing oil (with no friction modifier) for at least 15 h to allow appropriate running-in achieve a stabilised friction value, before using the selected oil under working conditions. Stabilisation of the engine is key to achieve reliable and constant frictional values, which occurs once asperities on the skirt and cylinder surfaces are partially polished.[42]

Single cylinder engine

In addition to the floating liner, motored single cylinder engine tests were done to produce liner samples for tribofilm analysis. The rig used in this work was a 0.5 l Hydra engine, manufactured by Ricardo UK Ltd (Figure 2). This single cylinder engine is based on the GM 2.0-litre Cavalier model. All auxiliary systems are independently controlled. Both oil and water temperatures were set at 90°C. The stroke in this case is 86 mm, with a cylinder bore of 86 mm. Full specifications can be found elsewhere.[43]

In this work, all tests using the Hydra engine were carried in motored mode. Using a dynamometer, the crankshaft was rotated at the set speed. For each lubricant tested, a new set of liners and piston rings were installed. The piston rings were made of ferrous alloys coated with phosphate (1st and 2nd rings) and chrome (oil-distribution ring). The liners were manufactured using ASTM A48 grade 30 cast iron. The engine was cleaned and flushed for at least 30 h to enable running-in of the surfaces using the oil free from MoDTC. Finally, tests were carried out under selected conditions using the oil to be analysed.

Oils and experiments

Oils

Two low viscosity oils were used in this study. Both are based on a group III basestock and an additive package containing detergents, dispersants, antioxidants and anti-wear additives. Oil 1: FF-2.1HTHS presents a polymeric viscosity modifier, whereas Oil 2: FF-1.7HTHS lacks this additive, presenting slightly lower viscosity under high speed and shear conditions. Further details are presented in Table 1.

An organic Molybdenum Dithiocarbamate Friction Modifier additive is blended onto these oils at different percentages (0.1 to 1 wt%), representing an overall Mo concentration of 100 to 1000 ppm.

Experiments

Oil 1 group was used in the floating liner system in both motored and fired modes, three concentrations of MoDTC were used (null, 0.5 wt% and 1 wt%). The main purpose of this set of experiments is to assess the influence of the combustion process on the friction reduction capability of the MoDTC additive. The effect of additive concentration was also considered. It is important to note that in this set of experiments the same liner was used for each oil under motored and fired conditions (run consecutively after stabilisation). No surface analysis techniques were carried out on this set, as it was unpractical to dismantle, analyse and assemble the liner between experiments (i.e., switching from motored to fired conditions with the same liner).

Oil 2 group was employed in two sets of experiments. On the one hand, a series of trials were run using the hydra engine in motored mode, to produce low friction tribofilms under a controlled set of conditions. On the other hand, AVL FRISC experiments were run using this oil group with a different concentration (ramping up from 0.1% to 0.3% then to 0.5% and finally to 0.7%) to extract frictional details and assess performance under different compositions, the engine was run for at least one hour with every change in oil concentration to ensure tribochemistry equilibrium with new MoDTC concentration is achieved. Both Hydra and AVL FRISC liners tested with Oil 2 group, were extracted for analysis in order to resolve the presence and distribution of low friction tribofilm and link the composition and distribution of the generated tribofilms to the friction performance under different engine conditions.

Specific conditions for both oils are reflected in Table 2. The engine speed in all experiments with AVL-FRISC was 1200 rpm, in Hydra a speed of 1300 rpm was used, as 1200 rpm caused undesirable vibrations. The configuration and dimensions between the AVL-FRISC and the Hydra engine are also slightly difference. This could represent local differences in the quantity and distribution of the species formed by tribochemistry. However, a qualitative comparison is thought to be valid, as temperatures and stresses are sufficiently high, and lubrication regime will be similar about the returning points, promoting efficient MoS_2 generation through tribochemistry. All fired tests in this work were carried out at an IMEP 6.5 bar. This entailed a Peak Combustion Pressure of 4 MPa at 14° CA.

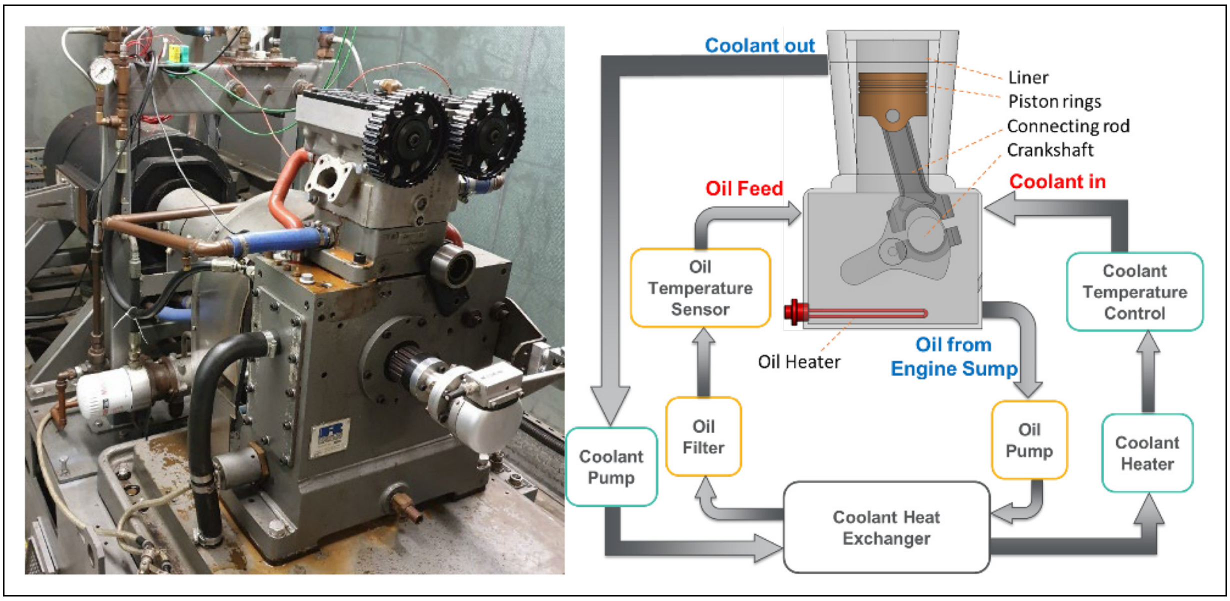

Figure 2. Picture of the single cylinder Hydra engine (left) and schematics describing the system components (right).

Table 1. Composition and fundamental physical characteristics of fully formulated oils.

	Oil 1 FF-2.1HTHS	Oil 2 FF-1.7HTHS
Polymeric Viscosity modifier (wt, %)	4	-
Base oil, group III (wt, %)	82	86
Kinematic viscosity of the base oil at 100°C (cSt)	4	3
HTHS at 150°C (cP)	2.1	1.7
Pressure-Viscosity Coefficient, GPa^{-1}	9.7	9.7
Dynamic viscosity at 90°C (η_o, Pa s)	$5.76 \cdot 10^{-3}$	$4.15 \cdot 10^{-3}$
Dynamic viscosity at 100°C (η_o, Pa s)	$4.76 \cdot 10^{-3}$	$3.42 \cdot 10^{-3}$

After the tests, liners were dry cut in stripes at key azimuthal positions and cleaned with compressed air to remove excess oil and cutting debris. Samples were slightly rinsed with heptane prior to surface analysis to minimise fluorescence and other negative effects.

Analysis

Frictional data

As described above, the AVL FRISC single cylinder rig enables high-speed acquisition and coupling with crankshaft angle. For all the experiments, friction force data (calibrated Fz after processing data from all sensors in all directions) was obtained every 0.2° CA. Raw data was averaged by taking mean values of 500 consecutive engine cycles to discard any singularity due to the engine cycle. These data processing was applied for both the additivated oil and the oil with no MoDTC. Once comparative data at every 0.2° CA was obtained for both oils, the friction reduction (FR) attributed to the addition of MoDTC, at every CA was calculated using the following expression:

$$FR(\%) = \left[\frac{F_{Ref\ Oil}}{F_{Test\ Oil}} - 1\right] \times 100$$

where $F_{Ref\ Oil}$ is the friction obtained with the Oil with no MoDTC and $F_{Test\ Oil}$ is the one obtained with Oil containing MoDTC run under the same conditions. Using this equation, if a positive FR value is obtained, a reduction in friction is achieved (i.e., $F_{Test\ Oil} < F_{Ref\ Oil}$). On the other hand, friction increases with the additive if the value is negative, $F_{Test\ Oil} > F_{Ref\ Oil}$. Friction Reduction curves were smoothed for clarity purposes.

Friction Mean Effective Pressure FMEP, is calculated by multiplying the friction force times the piston speed data at each point, multiplied by the time between two consecutive points and divided by the displacement volume. This quantity indicates the friction energy losses (in Joules) per volume displaced (in m^3), and it is measured in Pa.

Raman characterisation

To assess the amount and distribution of molybdenum compounds, Raman Microscopy was used. The device for this study was an InVia Raman Microscope (Renishaw Plc) equipped with 488 nm laser excitation source combined with a 2400 lines/mm grating and a refrigerated CCD detector to deliver a spectral resolution of 1 cm^{-1}. The spectrometer was coupled to a confocal Leica microscope mounting a 50x objective (numerical aperture of 0.5). A motored stage delivered a lateral resolution of 1 μm enabling accurate surface species maps.

The key application of Raman in this study is retrieving maps depicting the MoS_2 distribution on the surface. For

Table 2. Summary of experiments indicating oils and selected working conditions.

Engine	Mode	Liner	Lubricant	Speed (rpm)	IMEP (bar)
AVL-FRISC	Motored	AA-1	Oil 1	1200	-
		AA-2	Oil 1 + 0.5 wt% MoDTC		
		AA-3	Oil 1 + 1 wt% MoDTC		
	Fired	AA-1	Oil 1	1200	6.5
		AA-2	Oil 1 + 0.5 wt% MoDTC		
		AA-3	Oil 1 + 1 wt% MoDTC		
Hydra	Motored	H-1	Oil 2 + 0.3 wt% MoDTC	1300	-
		H-2	Oil 2 + 0.5 wt% MoDTC		
		H-3	Oil 2 + 0.7 wt% MoDTC		
AVL-FRISC	Fired	AB-1	Oil 2→+0.1→+0.3 →+0.5→+0.7 wt% MoDTC	1200	6.5
		AB-2	Oil 2→+0.5 wt% MoDTC		

this purpose, several 40 × 30 μm (Figure 3(b)) areas were selected along the longitudinal axis, covering the top dead centre, bottom dead centre and mid-stroke areas (as shown in Figure 3(a)). For each of these maps a grid comprising points spaced 1.5 μm in both X and Y directions was programmed using Renishaw WiRE software. This spacing was slightly larger than that of the laser spot size. Raman analysis was performed on each point, by irradiating the sample with the laser, filtered down to 1 mW for 8 s. Each spectrum was processed by eliminating cosmic ray outliers and correcting the fluorescent background. Then, the maximum Raman intensity (i.e., counts) around the MoS_2 A_{1g} vibration mode peak (410 cm^{-1}) was recorded. Raman maps are displayed using a colour code depending on the number of counts. A threshold count of 50 was established to determine the existence of MoS_2 on a particular spot, any Raman intensity at 410 cm^{-1} under this value will display no colour on the MoS_2 Raman maps.

X-Ray photoelectron spectroscopy

In order to resolve molybdenum compounds formed on the cylinder tribofilm under fired conditions, X-Ray Photoelectron Spectroscopy (XPS) was used. XPS analysis was performed with a Thermo NEXSA spectrometer (Thermo Electron, USA). The X-ray excitation was the Al-Kα line at 1486.7 eV and a spot size of 400 μm was selected. The detection of the photoelectrons was perpendicular to the surface and high-resolution spectra of the C1 s, O1 s, P2p, S2p, Zn2p, Ca2p, Mo3d, N1 s and Fe2p core levels were obtained to resolve the tribofilm composition. The S2p spectra were fitted to obtain the sulphide/sulphate ratio and relative binding energy positions. The S2p results were then used to fit the S2 s spectra (which are superposed to Mo3d spectra) to accurately resolve the Mo chemical environment.

Results and discussion

The effect of the combustion on friction performance

Figure 4(a) shows the frictional behaviour of Oil 1 group containing two different MoDTC concentrations. As expected, for every lubricant, friction forces remain lowest at mid-stroke areas, showing a sharp rise when approaching returning points (either the TDC or the BDC). This sharp rise is found in previous floating liner systems, and it is attributed to the transition from the elastohydrodynamic to the mixed/boundary lubrication regimes.[41,44–46] As expected, at returning points (CA = −360°, −180°, 0°, 180° and 360°) the friction force is close to zero due to the change of velocity and force directions. Another important fact observed in Figure 4(a) is the clear friction reduction achieved when MoDTC is blended to Oil 1 around TDC and BDC areas.

Looking at the friction reduction values (Figure 4(b) to (e)), FR between 90% to 240% is achieved at both TDC and BDC areas. No clear differences could be observed between 0.5% and 1% MoDTC concentrations, suggesting an effective boundary friction reduction on both occasions. At the mid-stroke area, there is a positive FR of about 30% in ascending strokes (compression and exhaust at Figure 4(c) and (e)) and a negative FR of about −20% in descending strokes (intake and expansion at Figure 4(b) and (d)). This is interesting as at mid-stroke, little or no FR values are expected as the oils tested have the same rheological properties. These differences can be attributed to assembly differences and components geometry differences, which could potentially cause asperity contact even at mid-stroke.[45] In any case, significant friction reduction in the vicinity of the returning points is evident.

As for the frictional behaviour in fired conditions, similar friction shape profiles are found with respect to the ones obtained with motored tests, i.e., low friction plateau mid-stroke and sharp friction increase around returning points (Figure 5(a)). One aspect to consider is that a friction spike is registered at 5 to 30° CA, representing a sharp decrease leading to close to zero or negative friction force values followed by a sharp increase. This feature is also reported in other works using similar floating liner test configurations.[45,47,48] It is attributed to a stick-slip effect due to the combination of a downward motion of the piston with a downward motion of the liner attributed to a sudden expansion of the seal following the combustion produced in the chamber at the beginning of the expansion stroke.[41] Under the same engine load and speed, this spike is produced in the same

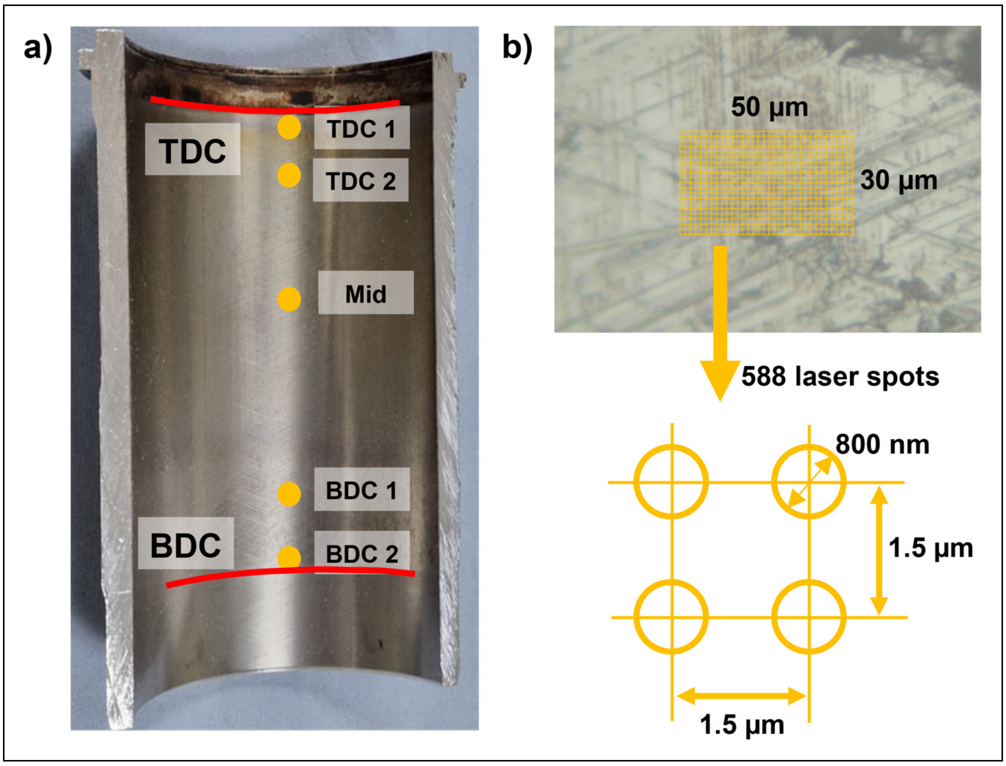

Figure 3. a) Half liner cut for analysis showing key areas for analysis of the single cylinder. b) area grids used for Raman mapping.

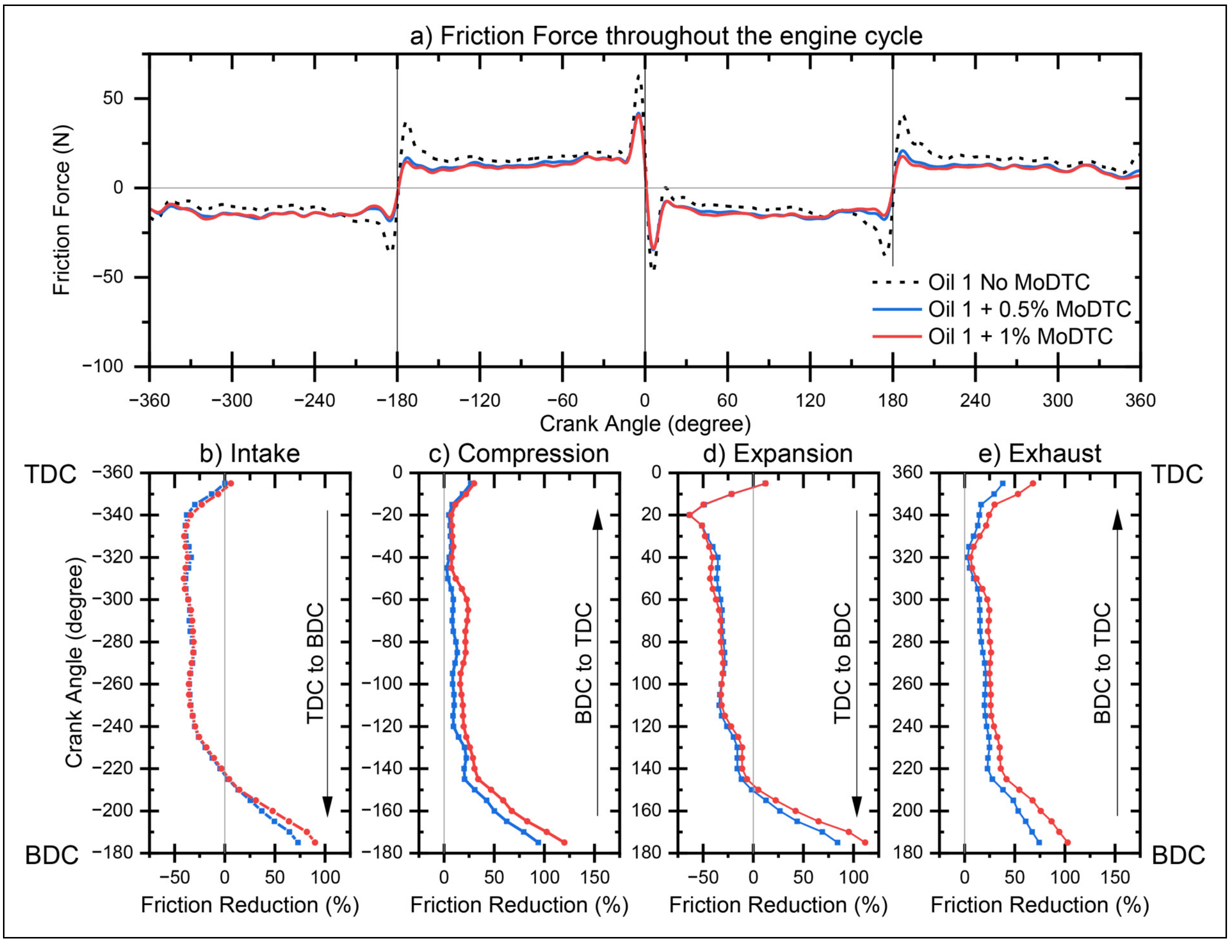

Figure 4. Friction analysis of Oil 1 (HTHS 2.1). Motored Tests. 1200 rpm. a) Friction force as a function of the crankshaft angle for Reference Oil 1, Oil 1 + 0.5% MoDTC and Oil1 + 1% MoDTC. b) to e) Friction reduction as a function of the crankshaft angle achieved by Oil + 0.5% MoDTC and Oil + 1% MoDTC during the Intake, Compression, Expansion and Exhaust strokes.

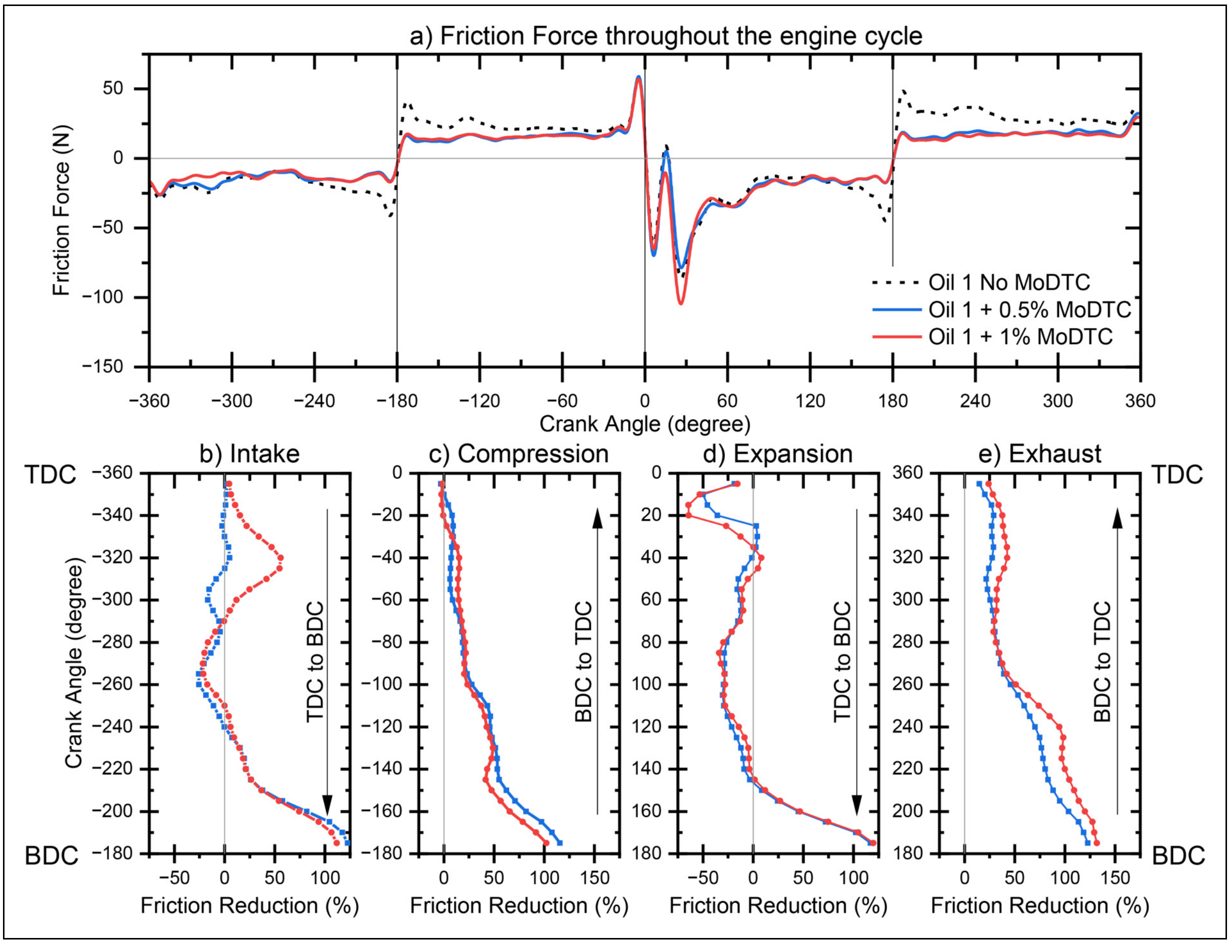

Figure 5. Friction analysis of Oil 1 (HTHS 2.1). Fired Tests. 1200 rpm. IMEP 6.5 bar a) Friction force as a function of the crankshaft angle for Reference Oil 1, Oil 1 + 0.5% MoDTC and Oil1 + 1% MoDTC. b) to e) Friction reduction as a function of the crankshaft angle achieved by Oil + 0.5% MoDTC and Oil + 1% MoDTC during the Intake, Compression, Expansion and Exhaust strokes.

crankshaft angle point, leading to usable FR data in this area. Another key observation is that, as a contrast to motored tests, large friction force differences are only observed at BDC areas, and not around TDC ones.

Looking into the FR values, Figure 5(b) to (e), confirm a friction reduction of up to 150% in BDC, whereas no significant FR was achieved in TDC, especially when compared to FR values calculated at mid-stroke. Similarly to motored tests, there is a tendency to have negative FR values, i.e., friction increase at mid-stroke in descending strokes (Figure 5(b) and (d)) and corresponding positive FR values mid-stroke in ascending ones (Figure 5(c) and (e)) which again is attributed to potential differences in liners, assemblies and ambient conditions. As with motored tests, there are no outstanding differences between Oil 1 + 0.5% and Oil 1 + 1%, signifying that at both concentrations, the MoDTC demonstrates the same level of effectiveness at the BDC areas and lack of effectiveness at the TDC/mid-stroke ones.

The effect of MoDTC concentration and viscosity on friction performance

Figure 6(a) illustrates the frictional behaviour of Oil 2 containing a range of MoDTC concentrations (0.1, 0.3, 0.5 and 0.7%), showing the usual plateau at mid-stroke combined with sharp friction force peaks close to returning points. When comparing these results to those of Oil 1 (Figure 5(a)), small frictional force differences are found. In general, slightly higher friction forces are found in all returning points, whereas mid-stroke values are similar. This suggest that the viscosity change from 2.1 to 1.7 leads to slightly harsher contact at the returning points, without a considerable gain in terms of hydrodynamic friction losses in the mid-stroke area. With regards to the effect of MoDTC concentration, values of 0.3% or above show similar behaviour, whereas 0.1% MoDTC oil matches the trend of the reference oil.

Investigating the FR along the engine cycle, considerable FR is achieved in every stroke around the BDC for concentrations above 0.1%, whereas 0.1% virtually shows no FR. The results of this test confirm that in a real engine tribological system there is a threshold of MoDTC concentration above which there will a significant tribological advantage, but below this threshold no effect can be observed. This agrees with previous observations on benchtop tribometer studies whereby a working/non-working condition is achieved at a certain MoDTC concentration and increasing it further has little impact on the friction value.[13,29] The main gains of an

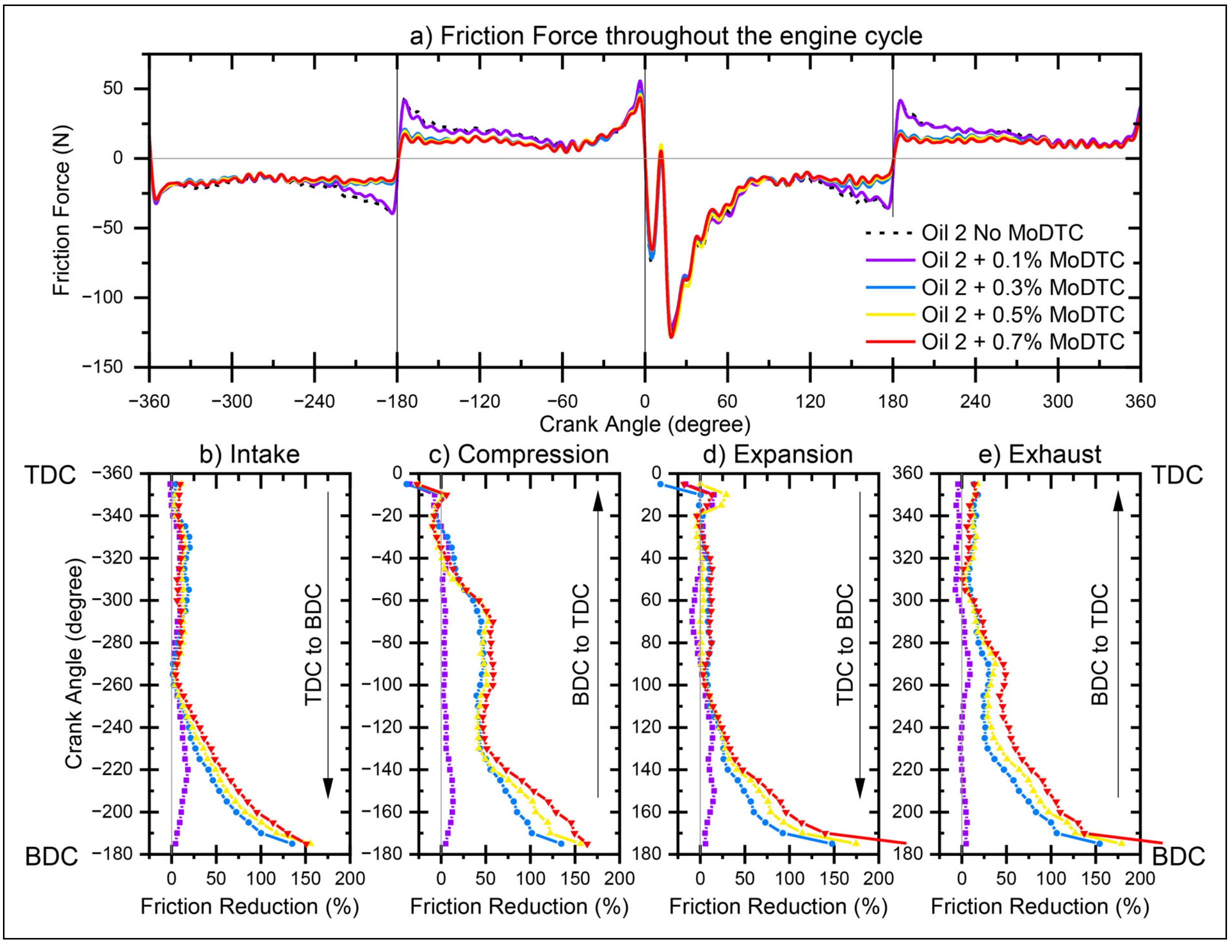

Figure 6. Friction analysis of Oil 2 (HTHS 1.7). Fired Tests. 1200 rpm. IMEP 6.5 bar a) Friction force as a function of the crankshaft angle for Reference Oil 2, Oil 2 + 0.1 to 0.7% MoDTC. b) to e) Friction reduction as a function of the crankshaft angle achieved by Oil 2 + 0.1% to 0.7% MoDTC during the Intake, Compression, Expansion and Exhaust strokes.

increased concentration of MoDTC over a certain threshold value are the expanded range of conditions where the formulation will deem effective and the durability of the FM formulation.[13,14]

Noteworthily, no statistically meaningful positive FR values are obtained in the mid-stroke area for any of the lubricants (Figure 6(b) to (e)). This confirms that the use of the same conditioned liner under equal ambient conditions will produce accurate data. Another interesting fact is that, during the piston ascending strokes (Figure 6(c) and (e)), FR is also produced in the mid-stroke area, suggesting that some degree of asperity-to-asperity contact is produced. Differences in the nature of the mid-stroke contact between ascending (Figure 6(c) and (e)) and descending (Figure 6(b) and (d)) strokes can be attributed to secondary motion of the piston.[40]

MoS_2 distribution on liners

Figure 7 illustrates how MoS_2 is distributed on the liner surface after a motored test is carried out under moderate speed (1300 rpm). In general, MoS_2 is formed at both returning points, with more presence around the BDC. The presence of MoS_2 at the topmost part of the TDC is limited. This could be related to thermal effects (high temperature is achieved during the end of the compression cycle even in motored tests), or harsh and short time contact between the 1st compression ring and the liner. Similar findings have been found in full engine motored tests where MoS_2 was found several mm below the TDC, at the area where the oil distribution ring would change direction.[39] MoS_2 is also observed to some extent in the mid-stroke area, where local asperity-to-asperity contact may produce MoS_2. Another possibility is that MoS_2 is dragged from the BDC area by the action of the reciprocating movement of the piston. Following expectations, a slightly wider deposition of MoS_2 was produced as the MoDTC concentration increases in the formulation.

Analysis on fired tests using similar oils depicts a different scenario. As seen in Figure 8, MoS_2 is formed at the BDC area, whereas no MoS_2 is present at mid-stroke and very little MoS_2 is formed in the vicinity of the TDC. These key differences in terms of MoS_2 distribution correlate well with the frictional behaviour, and more specifically, with the friction reduction achieved as a function of the crankshaft angle, whereby in motored tests, friction reduction is achieved in both returning points (MoS_2 is present around both returning points), but in fired tests, friction reduction is only achieved when the piston

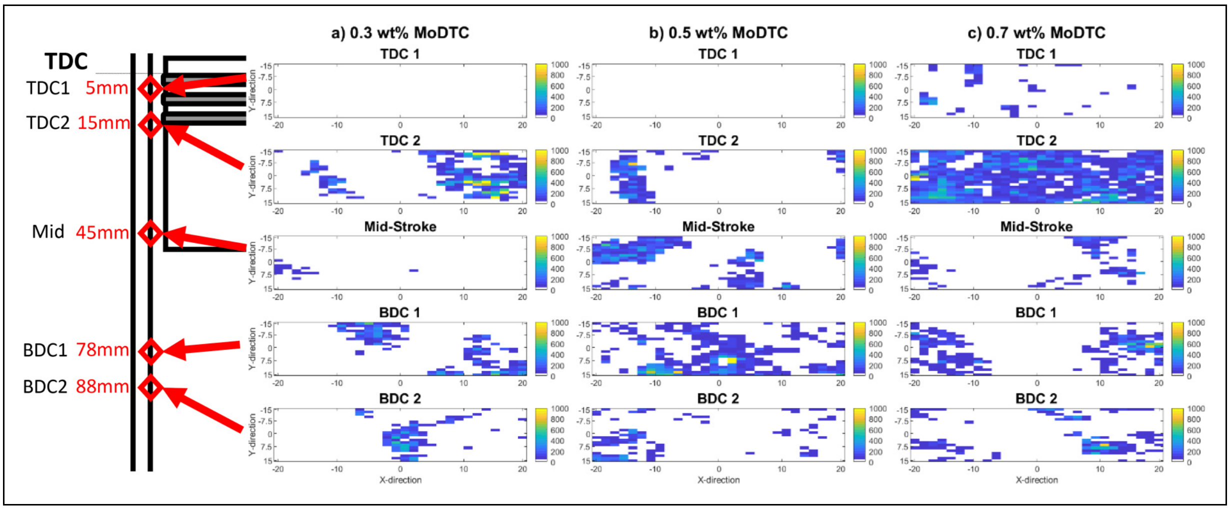

Figure 7. MoS_2 Raman map distribution at selected positions along the stroke after hydra engine motored tests using Oil 2 (HTHS 1.7) group. 1300 rpm: a) Oil 2 + 0.3% MoDTC b) Oil 2 + 0.5% MoDTC c) Oil 2 + 0.7% MoDTC. Colours indicate Raman intensity in counts.

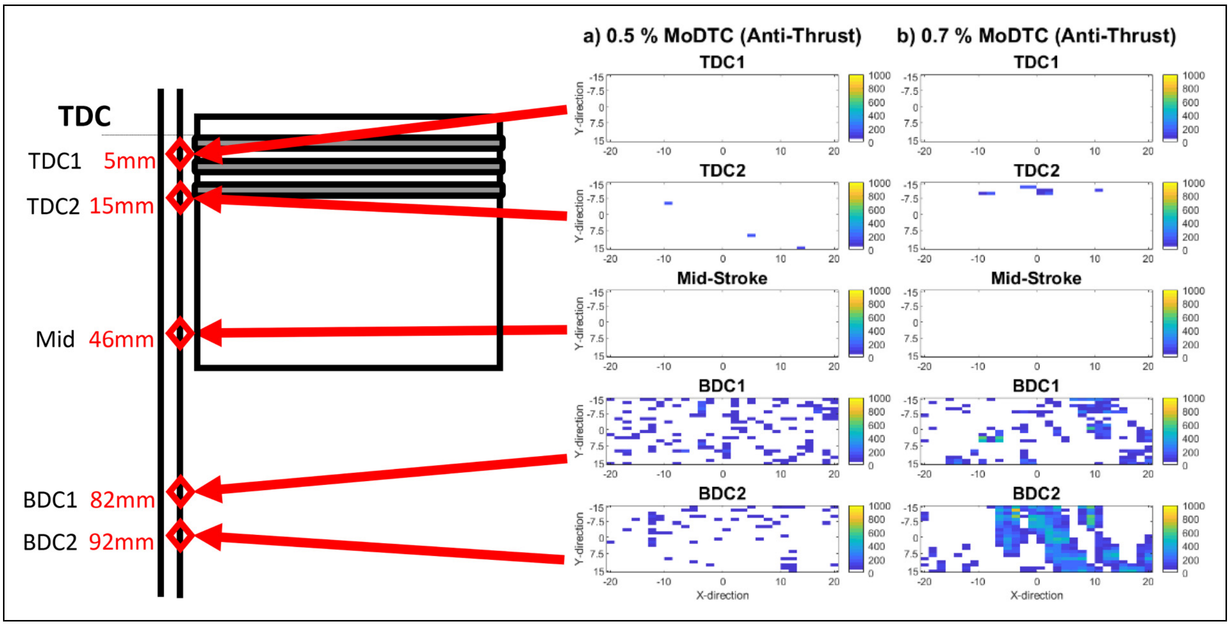

Figure 8. MoS_2 Raman map distribution at selected positions along the stroke after AVL FRISC fired tests using Oil 2 (HTHS 1.7) group. 1200 rpm: a) Oil 2 + 0.5% MoDTC b) Oil 2 + 0.7% MoDTC.

approaches the BDC area (MoS_2 is substantially present only in BDC area).

What is common in both configurations is that the larger the concentration of MoDTC in the oil, the larger the amount of MoS_2 on the surface. This larger distribution of MoS_2 with MoDTC concentration does not necessarily translate to a further friction reduction. An explanation can be found in the work carried out by Xu et al.,[37] where authors determined from tribological bench tests that once a certain MoS_2 coverage value is attained no further reduction is achieved in the system.

Raman analysis helps us understand how MoS_2 is formed on the liner, and what the role of combustion is, but uncertainty remains about the mechanisms that hinder the effective formation of an MoS_2 containing tribofilm at the TDC area. To discern the molybdenum species formed along the liner and resolve the tribochemistry mechanisms of MoDTC, XPS analysis of AVL FRISC fired engine test at 1200 rpm and 6.5 bar IMEP using the Oil 2 + 0.7% MoDTC is shown in Figure 9. Peak deconvolution shows the presence of Mo (IV) species corresponding to reduced MoS_2 in the BDC area of the liner.

The quantification analysis shown in Figure 10, depicts a larger presence of molybdenum species in the BDC area than in the TDC area. MoS_2 is only found in the BDC area (with larger presence further away from the combustion chamber), confirming the results obtained by Raman

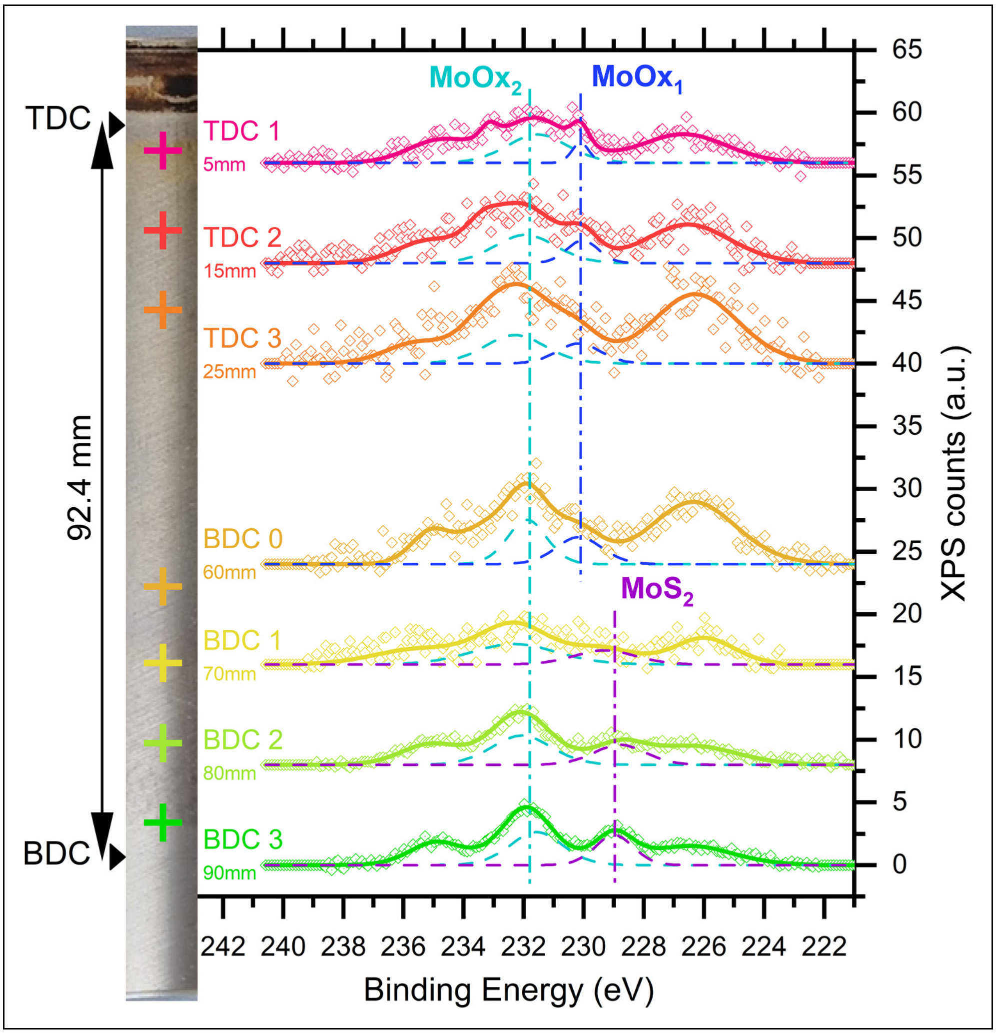

Figure 9. XPS analysis showing relevant Molybdenum peaks at key positions along the stroke of the AVL FRISC liner tested with Oil 2 + 0.7% MoDTC (1200 rpm, 6.5bar). $MoOx_2$, $MoOx_1$ and MoS_2 Mo3d5/2 fitted peaks are represented in dashed lines.

spectroscopy. Higher Mo oxidation states (named $MoOx_2$ in this work) are present throughout the stroke. These species would be related to Mo (VI) attributable to MoO_3, or more likely to $FeMoO_4$ which plays a fundamental role in the tribochemistry of MoDTC to deliver MoS_2.[17] More remarkable is the presence of partially oxidised molybdenum compounds (denoted by $MoOx_1$) instead of the fully reduced MoS_2 compound. These species show an intermediate oxidation state and most likely consist of MoS_xO_y compounds arising from partial oxidation of MoS_2,[49] or incomplete reduction to MoS_2 from MoDTC. Regardless of the driving mechanism, it is evident that the harsh temperature and oxidating conditions in the vicinity of the TDC severely impact the composition of the tribofilm.

Energy savings

A key outcome derived from the results is that the unique conditions occurring during the combustion phase do play a negative role in MoDTC tribochemistry and low friction tribofilm formation, limiting its potential friction benefits in boundary lubrication occurring on the piston-liner interface. Moreover, friction energy losses in the piston-cylinder system are majorly attributed to the mid-stroke parts of the cycle, where high speeds (displacement per unit time) will exacerbate the effect of friction reduction. As mid-stroke piston-cylinder contact tends to occur in the hydrodynamic regime, questioning whether MoDTC tribochemistry in boundary contact is sufficient to have a significative impact on energy losses remains.

Figure 11 shows that the presence of MoS_2 at both returning points has a moderate impact on FMEP in motored tests using Oil 1, with an overall FMEP reduction of 3 to 6% (for 0.5% and 1% MoDTC, respectively). Despite the negative effect of combustion, an overall FMEP reduction of more than 20% is achieved in fired tests. This can be attributed to the pressure and radial forces the combustion generates over the engine components, which promotes a harsher contact between the piston and the cylinder and a boundary or mixed lubrication contact over a wider span of the stroke, especially when low viscosity oils are used.[50] Breaking down FMEP to different areas of the stroke, it can be observed

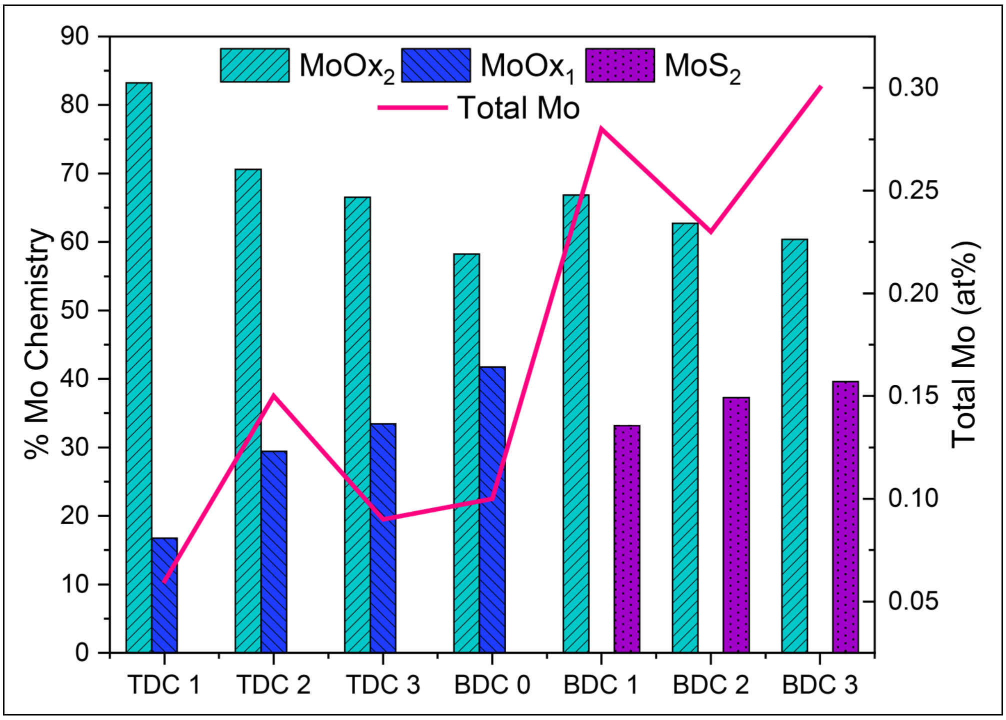

Figure 10. XPS analysis showing relevant Molybdenum peaks at key positions along the stroke of the AVL FRISC liner tested with Oil 2 + 0.7% MoDTC (1200 rpm, 6.5bar).

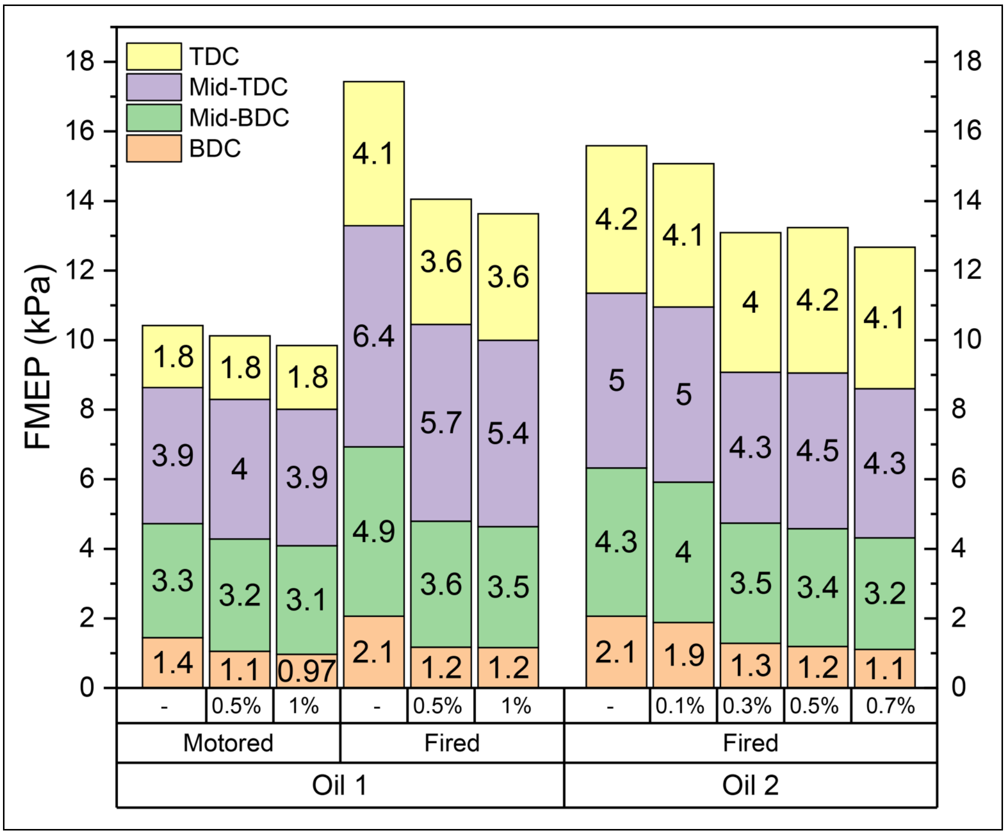

Figure 11. FMEP in kPa for Oil 1 (motored and fired tests) and Oil 2 (fired tests), and contribution to FMEP from BDC (−45° to 45° about BDC), low mid-stroke (−90° to −45° and 45° to 90° about BDC), high mid-stroke (−90° to −45° and 45° to 90° about TDC) and TDC (−45° to 45° about TDC).

that, for oil 1, only close contact around BDC generates a significant FMEP reduction in motored tests, but in fired tests, a reduction is apparent along the entire stroke, highlighting the contribution of the bottom part of the stroke to this achievement. The less viscous Oil 2 presents a slightly lower FMEP under the same conditions as those of Oil 1, with a smaller FMEP contribution from the mid-stroke area (purple and green bars) and a slightly higher contribution from the returning points (yellow and orange bars). With the addition of MoDTC, an overall FMEP reduction of about 15% is obtained, in agreement with the findings of Tomanik et al. in an experiment under similar speed and loading conditions.[51] The additive remarkably contributed, not only close to the BDC area but also at mid-stroke range. On this occasion, regardless of the MoDTC, FMEP is not reduced in the vicinity of the TDC, due to the conditions leading to the absence of MoS_2 at the top part of the cylinder, in agreement with Raman and XPS findings.

As previously mentioned, a threshold of MoDTC needs to be overcome to achieve effective frictional gains, with no further beneficial effect on friction as the concentration increases. Selecting a higher concentration of MoDTC would be required to account for the depletion of the additive,[52] and ensure an effective friction reduction between designed service intervals in the final application. Geometries, working conditions and materials need to be taken into account for the determination of the optimal additive concentration.[10] It is also noteworthy that the addition of MoDTC minimised the effect of reducing the viscosity, in agreement with the findings obtained by Ito et al. for diesel engines.[7] In this study, the lowest viscosity oil containing 0.7% MoDTC exhibited the best frictional performance under moderate load and low speed fired conditions.

Conclusions

Frictional data from floating liner rig combined with advanced surface analysis provided key insights on MoDTC tribochemistry and its effect on friction under real engine conditions. These are listed as follows:

- In motored tests, MoDTC decomposes to MoS_2 at both returning points (TDC and BDC). This translates to moderate FMEP reduction, as friction reduction is only produced when piston speeds are low.
- In fired tests, MoDTC decomposes to MoS_2 only at the BDC area. No fully crystalline MoS_2 is present at the TDC, but oxidised molybdenum species are present instead. The presence of MoS_2 at the bottom part of the cylinder suffices to provide remarkable FMEP reduction throughout the entire cycle, with a major contribution when the piston is located at the lower half of the cylinder. This FMEP reduction is attributed to harsh conditions under fired conditions and low viscosity oils, which expands the range along the stroke where boundary lubrication occurs, enabling friction reduction by MoDTC tribochemistry.
- Piston-cylinder tests evidence the necessity of a minimum percentage of MoDTC to trigger MoDTC tribochemistry under certain conditions in agreement with results obtained on benchtop tribometers. A higher concentration above the minimum required provides a higher MoS_2 coverage in the areas where boundary lubrication occurs, but this higher coverage does not entail further FMEP reduction, demonstrating that a friction reduction effect is achieved when a certain quantity of asperities is appropriately covered.

These findings set a unique framework for the development of low viscosity oils containing MoDTC friction modifiers, tailored for internal combustion engines subject to specific working and durability requirements.

Declaration of conflicting interests

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

The authors received no financial support for the research, authorship, and/or publication of this article.

ORCID iDs

Abdullah Nashmi Alenezi https://orcid.org/0009-0002-8481-2120
Cayetano Espejo https://orcid.org/0000-0001-7139-3807
Quentin Arnoux https://orcid.org/0000-0002-3677-9787
Ardian Morina https://orcid.org/0000-0001-8868-2664

References

1. IEA. World Energy Outlook 2023. Paris 2023. Available from: https://www.iea.org/reports/world-energy-outlook-2023.
2. IPCC. *Climate change 2023: synthesis report*. Geneva: Switzerland: IPCC, 2023. p. 35–115. Available from: https://doi.org/10.59327/IPCC/AR6-9789291691647.
3. Holmberg K and Erdemir A. The impact of tribology on energy use and CO_2 emission globally and in combustion engine and electric cars. *Tribol Int* 2019; 135: 389–396.
4. Blau PJ. Friction in internal combustion engines. In: Wang QJ and Chung Y-W (eds) *Encyclopedia of tribology*. Boston, MA: Springer US, 2013, pp.1322–1325. https://doi.org/10.1007/978-0-387-92897-5_192.
5. Dellis P. On the effect of temperature in friction force measurements for a simplified piston cylinder set-up: squeeze film combined with minimum oil film thickness measurements and viscosity index effect. *Proceedings of the Institution of Mechanical Engineers, Part J* 2023; 237: 1723–1742.
6. Taylor R. Squeeze film lubrication in piston rings and reciprocating contacts. *Proceedings of the Institution of Mechanical Engineers, Part J* 2015; 229: 977–988.
7. Ito A, Chubachi Y, Yamamoto T, et al. A Study on Effects of Low Viscosity Engine Oil and MoDTC on Piston Friction Losses in a DI Diesel Engine. *SAE Technical Papers* 2015: 2015-01-2044. https://doi.org/10.4271/2015-01-2044.

8. SAE International. J300_202405 Engine Oil Viscosity Classification. 2024. https://doi.org/10.4271/J300_202405
9. Taylor OP, Pearson R, Stone R, et al. Tribological Behavior of Low Viscosity Lubricants in the Piston to Bore Zone of a Modern Spark Ignition Engine. SAE 2014 International Powertrain, Fuels & Lubricants Meeting. Birmingham, UK. 2014. SAE Technical Paper 2014-01-2859. https://doi.org/10.4271/2014-01-28592014-01-2859.
10. Sagawa T, Katayama T, Suzuki R, et al. Development of GF-5 0W-20 Fuel-Saving Engine Oil for DLC-Coated Valve Lifters. *SAE Technical Papers* 2014: 2014-01-1478. https://doi.org/10.4271/2014-01-1478.
11. Tamoto Y, Kido M and Murata H. Possibilities of Ultra Low Viscosity Fuel Saving Gasoline Engine Oil. *SAE Technical Papers* 2004: 2004-01-1936. https://doi.org/10.4271/2004-01-1936.
12. Liu Y, Han JH, Wang T, et al. Tribochemical reaction and wear mechanism of MoDTC based friction modifier. *Tribol Int* 2022; 165: 107302. https://doi.org/10.1016/j.triboint.2021.107302.
13. Graham J, Spikes H and Korcek S. The friction reducing properties of molybdenum dialkyldithiocarbamate additives: part I - factors influencing friction reduction. *Tribol Trans* 2001; 44: 626–636.
14. Graham J, Spikes H and Jensen R. The friction reducing properties of molybdenum dialkyldithiocarbamate additives: part II - durability of friction reducing capability. *Tribol Trans* 2001; 44: 637–647.
15. Khaemba DN, Jarnias F, Thiébaut B, et al. The role of surface roughness and slide-roll ratio on the decomposition of MoDTC in tribological contacts. *J Phys D Appl Phys* 2017; 50: 085302.
16. Khaemba DN, Neville A and Morina A. A methodology for Raman characterisation of MoDTC tribofilms and its application in investigating the influence of surface chemistry on friction performance of MoDTC lubricants. *Tribol Lett* 2015; 59: 1–17.
17. Khaemba DN, Neville A and Morina A. New insights on the decomposition mechanism of molybdenum DialkyldiThioCarbamate (MoDTC): a Raman spectroscopic study. *RSC Adv* 2016; 6: 38637–38646.
18. Morina A, Zhao H and Mosselmans JFW. In-situ reflection-XANES study of ZDDP and MoDTC lubricant films formed on steel and diamond like carbon (DLC) surfaces. *Appl Surf Sci* 2014; 297: 167–175.
19. Trindade ED, Zuleta Durango A and Sinatora A. Friction and wear performance of MoDTC-containing and ester-containing lubricants over steel surfaces under reciprocating conditions. *Lubr Sci* 2015; 27: 217–229.
20. Al Kharboutly M, Veryasov G, Gaval P, et al. Mo(VI) dithiocarbamate with no pre-existing mo–S–mo core as an active lubricant additive. *Tribol Int* 2021; 154: 106690. https://doi.org/10.1016/j.triboint.2020.106690.
21. Barnes AL, Morina A, Andrew RE, et al. The effect of additive chemical structure on the tribofilms derived from varying molybdenum-sulfur chemistries. *Tribol Lett* 2021; 69: 134. https://doi.org/10.1007/s11249-021-01493-z.
22. Gorbatchev O, De Barros Bouchet MI, Martin JM, et al. Friction reduction efficiency of organic Mo-containing FM additives associated to ZDDP for steel and carbon-based contacts. *Tribol Int* 2016; 99: 278–288.
23. Hu J-Q, Wei X-Y, Dai G-L, et al. Tribological behaviors and mechanism of sulfur- and phosphorus-free organic molybdate ester with zinc dialkyldithiophosphate. *Tribol Int* 2008; 41: 549–555.
24. de Barros'Bouchet MI, Martin JM, Le-Mogne T, et al. Boundary lubrication mechanisms of carbon coatings by MoDTC and ZDDP additives. *Tribol Int* 2005; 38: 257–264.
25. Morina A, Neville A, Priest M, et al. ZDDP And MoDTC interactions in boundary lubrication—The effect of temperature and ZDDP/MoDTC ratio. *Tribol Int* 2006; 39: 1545–1557.
26. Morina A, Neville A, Priest M, et al. ZDDP And MoDTC interactions and their effect on tribological performance – tribofilm characteristics and its evolution. *Tribol Lett* 2006; 24: 243–256.
27. Costello MT and Urrego RA. Study of surface films of the ZDDP and the MoDTC with crystalline and amorphous overbased calcium sulfonates by XPS. *Tribol Trans* 2007; 50: 217–226.
28. Pereira G, Lachenwitzer A, Munoz-Paniagua D, et al. Nanoscale chemistry and mechanical properties of tribofilms on al–si alloy (A383): interaction of ZDDP, calcium detergent and molybdenum friction modifier. *Tribol Mater Surf Interfaces* 2007; 1: 4–17.
29. Vaitkunaite G, Espejo C, Wang C, et al. MoS_2 tribofilm distribution from low viscosity lubricants and its effect on friction. *Tribol Int* 2020; 151: 106531. https://doi.org/10.1016/j.triboint.2020.106531.
30. de Feo M, de BarrosBouchet MI, Minfray C, et al. MoDTC lubrication of DLC-involving contacts. *Impact of MoDTC Degradation. Wear* 2016; 348–349: 116–125.
31. Espejo C, Thiébaut B, Jarnias F, et al. MoDTC tribochemistry in steel/steel and steel/diamond-like-carbon systems lubricated with model lubricants and fully formulated engine oils. *J Tribol* 2019; 141: 012301–12.
32. Haque T, Morina A and Neville A. Influence of friction modifier and antiwear additives on the tribological performance of a non-hydrogenated DLC coating. *Surf Coat Technol* 2010; 204: 4001–4011.
33. Jiménez AE, Morina A, Neville A, et al. Surface interactions and tribochemistry in boundary lubrication of hypereutectic aluminium—silicon alloys. *Proc Inst Mech Eng Part J J Eng Tribol* 2009; 223: 593–601.
34. Kosarieh S, Morina A, Flemming J, et al. Wear mechanisms of hydrogenated DLC in oils containing MoDTC. *Tribol Lett* 2016; 64: 4.
35. Sugimoto I, Honda F and Inoue K. Analysis of wear behavior and graphitization of hydrogenated DLC under boundary lubricant with MoDTC. *Wear* 2013; 305: 124–128.
36. Vengudusamy B, Green JH, Lamb GD, et al. Behaviour of MoDTC in DLC/DLC and DLC/steel contacts. *Tribol Int* 2012; 54: 68–76.
37. Xu D, Wang C, Espejo C, et al. Understanding the friction reduction mechanism based on molybdenum disulfide tribofilm formation and removal. *Langmuir* 2018; 34: 13523–13533.
38. Garcia CE, Ueda M, Spikes H, et al. Temperature dependence of molybdenum dialkyl dithiocarbamate (MoDTC) tribofilms via time-resolved Raman spectroscopy. *Sci Rep* 2021; 11: 3621. https://doi.org/10.1038/s41598-021-81326-0.

39. Espejo C, Wang C, Thiébaut B, et al. The role of MoDTC tribochemistry in engine tribology performance. A Raman microscopy investigation. *Tribol Int* 2020; 150: 106366. https://doi.org/10.1016/j.triboint.2020.106366.
40. Vaitkunaite G, Espejo C, Thiébaut B, et al. Low friction tribofilm formation and distribution on an engine cylinder tested with MoDTC-containing low viscosity engine lubricants. *Tribol Int* 2022; 171: 107551. https://doi.org/10.1016/j.triboint.2022.107551.
41. Winklhofer E, Loesch S and Satschen S. High precision piston to liner friction measurement. JSAE Annual Congress (Spring). Yokohama: Proceedings of the JSAE Annual Congress. 2016. p. 1864–1869.
42. Meng Z, Zhang L and Tian T. Study of break-in process and its effects on piston skirt lubrication in internal combustion engines. *Lubr* 2019; 7: 98. https://doi.org/10.3390/lubricants7110098.
43. Mufti RA and Priest M. Theoretical and experimental evaluation of engine bearing performance. *Proc Inst Mech Eng Part J J Eng Tribol* 2009; 223: 629–644.
44. Oh H, Ha K-P and Min K. Development of a new measurement system for piston ring friction based on the floating liner method. *International Journal of Automotive Technology* 2023; 24: 1205–1211.
45. Tabata H, Kaneko N and Mihara Y. Improvement in accuracy of piston frictional force measurement using floating liner engine. *Tribol Online* 2017; 12: 141–146.
46. Walch S, Hick H, Edtmayer J, et al. Multimethod Concept for Continuous Wear-Analysis of the Piston Group. WCX World Congress Experience. Detroit, USA: SAE Technical Paper 2018-01-0839. 2018. https://doi.org/10.4271/2018-01-0839.
47. Furuhama S and Takiguchi M. Measurement of Piston Frictional Force in Actual Operating Diesel Engine. *SAE Technical Papers* 1979: 790855. https://doi.org/10.4271/790855.
48. Plettenberg M, Schäffer J, Edtmayer J, et al. A holistic Development Method Based on AVL FRISC as Enabler for CO_2 Reduction with Focus on Low Viscosity Oils. *SAE Technical Papers* 2020: 2020-01-1060. https://doi.org/10.4271/2020-01-1060.
49. Brown NMD, Cui N and McKinley A. An XPS study of the surface modification of natural MoS_2 following treatment in an RF-oxygen plasma. *Appl Surf Sci* 1998; 134: 11–21.
50. Merkle A, Wachtmeister G and Kunkel S. Analysis of the mixed friction in the piston assembly of a SI engine. *SAE International Journal of Engines* 2012; 5: 1487–1497.
51. Tomanik E, Fujita H, Sato S, et al. Investigation of PVD Piston Ring Coatings With Different Lubricant Formulations. *ASME 2017 Internal Combustion Engine Division Fall Technical Conference*. Seattle, Washington, USA. 2017. https://doi.org/10.1115/ICEF2017-3559.
52. Arai K, Yamada M, Asano S, et al. Lubricant technology to enhance the durability of low friction performance of gasoline engine oils. *SAE Technical Papers* 1995: 952533. https://doi.org/10.4271/952533