

This is a repository copy of *Extraction and tribological investigation of top piston ring zone oil from a gasoline engine*.

White Rose Research Online URL for this paper:

<https://eprints.whiterose.ac.uk/4871/>

---

**Article:**

Lee, P.M., Priest, M., Stark, M.S. [orcid.org/0000-0002-2175-2055](https://orcid.org/0000-0002-2175-2055) et al. (4 more authors) (2006) Extraction and tribological investigation of top piston ring zone oil from a gasoline engine. *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology*. pp. 171-180. ISSN 1350-6501

<https://doi.org/10.1243/13506501JET148>

---

**Reuse**

Items deposited in White Rose Research Online are protected by copyright, with all rights reserved unless indicated otherwise. They may be downloaded and/or printed for private study, or other acts as permitted by national copyright laws. The publisher or other rights holders may allow further reproduction and re-use of the full text version. This is indicated by the licence information on the White Rose Research Online record for the item.

**Takedown**

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing [eprints@whiterose.ac.uk](mailto:eprints@whiterose.ac.uk) including the URL of the record and the reason for the withdrawal request.

*promoting access to White Rose research papers*



**Universities of Leeds, Sheffield and York**  
**<http://eprints.whiterose.ac.uk/>**

---

This is an author produced version of a paper published in Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology.

White Rose Research Online URL for this paper:  
<http://eprints.whiterose.ac.uk/4871/>

---

**Published paper**

Lee, P.M., Priest, M., Stark, M.S., Wilkinson, J.J., Lindsay-Smith, J.R., Taylor, R.I. and Chung, S. (2006) *Extraction and tribological investigation of top piston ring zone oil from a gasoline engine*. Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology, 220 (3). pp. 171-180.

<http://dx.doi.org/10.1243/13506501JET148>

---

# Extraction and tribological investigation of top piston ring zone oil from a gasoline engine

P M Lee<sup>1\*</sup>, M Priest<sup>1</sup>, M S Stark<sup>2</sup>, J J Wilkinson<sup>2</sup>, J R Lindsay Smith<sup>2</sup>, R I Taylor<sup>3</sup> and S Chung<sup>4</sup>

<sup>1</sup>Institute of Tribology, School of Mechanical Engineering, University of Leeds, Leeds, UK

<sup>2</sup>Department of Chemistry, University of York, York, UK

<sup>3</sup>Shell Global Solutions, Chester, UK

<sup>4</sup>Infineum UK Limited, Milton Hill, Abingdon, Oxfordshire, UK

*The manuscript was received on 13 September 2005 and was accepted after revision for publication on 15 February 2006.*

DOI: 10.1243/13506501JET148

**Abstract:** With tightening emission regulations, increased expected fuel economy, and longer drain intervals impacting on lubricant formulation, greater understanding of how oil degrades in an automotive engine is becoming ever more important. Equally significant is the effect that this degraded lubricant has on the tribological operation of the engine, particularly its overall internal friction and component wear.

In a previous paper, four tests to degrade oil in a single cylinder engine were reported (Lee, P. M. *et al.* The degradation of lubricants in gasoline engines: development of a test procedure to evaluate engine oil degradation and its consequences for rheology. In 31st Leeds-Lyon Symposium). These tests were set up such that the lubricating oil was degraded in the ring pack before returning to the sump, where it was sampled and chemical and rheological analysis undertaken. This paper reports the extension of this work using the same Hydra engine and describes how oil has additionally been extracted from the rear of the top piston ring during engine operation. This extracted oil has then been subjected to similar analysis as the sump oil samples in the previous tests, along with additional analysis to look at the tribological properties of the oil using tribometers.

The results clearly show significant differences in the rheological, tribological, and chemical properties of the fresh oil and used sump oil samples when compared with the top ring zone (TRZ) oil samples, particularly the effect of load on the levels of volatiles present in the TRZ samples and their effect on traction and friction coefficient values during tribological testing.

## Q1 Keywords:

## 1 INTRODUCTION

Increasing specifications and demands are being made on engine oil at the same time as tried and tested additives are being forced out of the formulators bank of options. There is therefore an ever increasing need to further understand how and why the lubricating oil degrades in an operating engine and how this affects the tribological behaviour of the engine. This need is further exacerbated

by the oil being required to have improved fuel economy properties and less volatility, while having increased engine protection from wear and corrosion for increasingly longer periods of time between drain intervals.

In a previous paper [1], a set of four tests looking at the degradation of the sump oil, due to contamination caused by the oil returning from the ring pack to the sump were reported. In the reported work, a number of rheological and chemical tests were undertaken on the sump oil in order to investigate the levels of degradation.

This paper reports the extension of that work by additionally sampling and testing oil from the top ring zone (TRZ) of the engine. A sampling system

\*Corresponding author: Institute of Tribology, School of Mechanical Engineering, University of Leeds, Leeds LS2 9JT, UK. email: efy7pml@leeds.ac.uk

has been devised, which allows oil to be extracted directly from the rear of the top piston ring into sample vials external to the engine while the engine is running at 1500 r/min. To investigate the effects of the degraded oil in the ring pack on the tribological performance of the engine and, therefore on the internal friction and wear of the rings and liner, these oils have been subjected to chemical, rheological, and tribological tests. This is the first time that such large quantities of oil (over 25 ml) have been sampled from a piston assembly of a gasoline engine and therefore the first time such samples have been subjected to such extensive analysis. The purpose of this work was to make initial in-roads into the tribological analysis of TRZ oils and look at a range of testing methods in order to guide future research.

## 2 THEORY

High operating temperatures near the combustion chamber (thermal oxidation) and interaction with the combustion gases that pass from the combustion chamber, through the rings, to the crankcase (blow-by gases) are the main constituents of oil degradation [2, 3]. As such, the vast majority of oil degradation occurs in the ring pack. If the sump oil is maintained at a temperature below that at which thermal degradation occurs, then the engine may be considered as a reactor (Fig. 1), where the bulk oil in the sump is contaminated by the degraded oil in the piston ring pack when it returns to the sump [4, 5].

The rate of bulk oil degradation in the sump is dependent upon the quantity of oil and its residence time in the ring pack and flowrates between the ring pack and the sump. Studies into lubricant TRZ residence times and flowrates for this engine have been reported in previous papers [6, 7] and more in-depth theory can be found in these papers and the paper reporting the previous work [1, 6, 7].

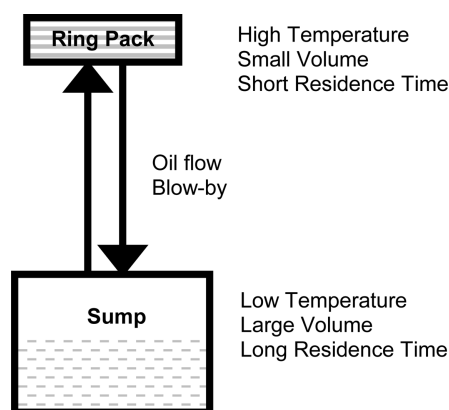


Fig. 1 Reactor model of an engine

## 3 EXPERIMENTAL WORK

### 3.1 Engine

A single cylinder Hydra gasoline research engine (Ricardo Consulting Engineers Limited) was used for this work. This engine is quarter of a 1998 cc in-line four cylinder GM Engine introduced into service in 1988 and the piston (AE reference 24024) and rings (AE reference R23490) are production parts used in this GM engine. The ring pack consists of three rings: top ring, oil scraper ring, and oil control ring. This single cylinder research engine has a displacement of 499.5 cc with two direct acting overhead camshafts: one operating two inlet valves, the other two exhaust valves. The engine is liquid cooled and naturally aspirated with indirect injection. The engine is located on a test bed with control over the valve timing, ignition timing, fuel injection event, throttle position, and oil and coolant temperatures. Connected to the engine is a solid-state dynamometer that either motors the engine or controls its fired speed under a set absorbed load. Data acquisition includes air to fuel ratio, engine load, and temperatures and pressures at various points on the engine. The maximum torque output from the engine when in this experimental set-up is 36 N m and the compression ratio is 10.25:1.

### 3.2 TRZ sampling system

TRZ sampling has previously been undertaken by a number of research establishments with heavy duty diesel and gasoline engines [4, 8, 9]; these have all been of older design than the Hydra engine. This method of extracting oil from the rear of a piston ring during engine operation is based on the theory that when the top ring is sitting on the lower flank the pressure differential between the entrance to the sample hole and the atmosphere forces some of the combustion gases, along with oil from around the sample hole down the pipe in the form of a mist. Towards the end of the combustion stroke, the top ring can lift and then oil and gas from the second land can enter the hole in the form of a mist. At the end of the sample pipe, this collective mist is then sprayed against the side of a collection vial where, upon contact, the liquids condense, collecting in the bottom of the vial, and the gases are extracted. This technique has now been successfully developed to work in the Hydra engine, having overcome the problems of increased engine speed, shorter faster strokes, and increased geometric restrictions. Due consideration was given to the intrusive nature of this method during its design. Tests showed that the quantity

of oil sampled was between 1.5 and 2.0 per cent of the oil flow through the ring pack as measured in previous work [7], and therefore unlikely to significantly change the residence time of the oil in the ring pack. In this experimental set-up, a 0.5 mm diameter hole was drilled in the thrust side of the top ring groove through to the inside of the piston where it was connected to a 1.59 mm external diameter PTFE tube. This flexible tube was then fed through a stainless steel sleeve down the connecting rod to the big end bearing. At the big end bearing, the tube was connected to a 4.76 mm external diameter tube that was axially restrained by being passed round a shaft before exiting through the side of the engine into the collection vial (Fig. 2).

### 3.3 Lubricant

For consistency between these tests and previous tests [1], the same fully formulated oil was used. Shell Helix Super SAE-15W/40 fully formulated lubricant was used. This lubricant is formulated using Group I base oils and meets recognized industry standard specification tests (API SH/CF, ACEA A2/B2-98) and will adequately lubricate engines requiring this oil performance standard. However, compared with lubricants meeting more modern industry standards or OEM-specific performance requirements (which may require the use of synthetic base oils), this oil is likely to have a lower oxidation performance. Higher levels of degradation were preferable in order to be able to analyse the degraded oil and increase the chance of having measurable differences between the test results within a relatively short test duration.

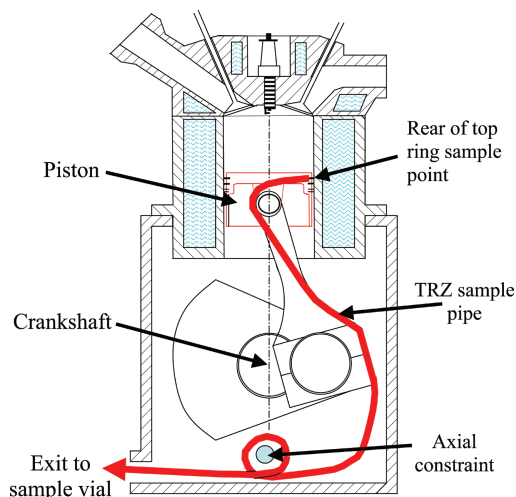


Fig. 2 Top ring zone (TRZ) sampling system

### 3.4 Engine oil samples

Table 1 gives the operating conditions and history of the six oil samples collected for this work. Because of the small quantities of oil sampled from the TRZ for each engine revolution, the collection of each TRZ sample took in the region of 40 h engine running. For this reason, the samples were highly precious and, only being in the region of 25 ml each, repeatability testing was only practical with the fresh and sump oil in order to maximize the range of tests undertaken.

### 3.5 Chemical analysis

The chemical tests carried out included field ionization-mass spectroscopy (FIMS), gas chromatography (GC), and Fourier transform Infrared (FTIR) spectroscopy of the lubricant samples.

#### 3.5.1 Field ionization-mass spectroscopy

FIMS was carried out in accordance with the generic test method TMC 521/04 (Shell Global Solutions, UK) in order to semiquantitatively determine the concentration of hydrocarbon types in terms of their carbon number and hydrogen deficiency. This involved using a magnetic sector instrument equipped with a field desorption/field ionization (FD/FI) interface using standard FI conditions for that instrument, ensuring that the source was kept as cool as practicable (i.e. about 30 °C) to minimize thermal fragmentation. The FD extraction voltage was 5 kV with extraction plate heating of 40 per cent. The interscan current was 40 mA and the emitter current 5 mA. The sample probe temperature was ramped from 40 to 400 °C using a two-stage sample crucible.

#### 3.5.2 Gas chromatography

A GC fitted with a flame ionization detector (FID) was used to analyse the quantity of volatiles present in the lubricant samples. A marker was added to the lubricant sample and then analysed using a Zebtron ZB-5 column.

Table 1 Conditions for six oil samples collected

Oil sample name	Oil sample conditions
33% load TRZ	33% maximum engine load at 1500 r/min
50% load TRZ	50% maximum engine load at 1500 r/min
75% load TRZ	75% maximum engine load at 1500 r/min
First 15 min	First 15 min from cold start at 1500 r/min
Fresh oil	Fresh Shell Helix Super 15W-40
40 h sump oil	Used sump oil after 40 h at 50% maximum engine load 1500 r/min

### 3.5.3 Fourier transform infrared spectroscopy

FTIR spectroscopy was undertaken to quantitatively determine the degree of oxidation of the lubricant by monitoring the concentration of carbonyl-containing species present at wave numbers 1690–1750  $\text{cm}^{-1}$ . The FTIR method for the quantification of carbonyl content was calibrated using a range of different carbonyl compounds likely to be in the oxidized oil, namely, ketones, carboxylic acids, esters, and lactones [10, 11]. Integrated absorptions were used for the calibrations and not peak intensities, as the former proved to be very similar for the different carbonyl-containing compounds examined [6]. Fresh Shell Helix Super was used as the background reference and carbonyl concentrations were measured relative to this. The results of the GC analysis were used to correct the carbonyl concentration measured by FTIR due to the samples being diluted by the volatiles derived from the fuel and combustion products. These corrected values are reported in this paper. A Nicolet 410 Impact Spectrophotometer was used; the IR cell features calcium fluoride windows and uses a 1 mm path length.

During the tribological tests described in section 3.7, samples of oil were tested at 100 °C for up to 4 h, begging the question whether the test would degrade the oil samples. For this reason, a small quantity of each oil sample was heated in a test tube open to the atmosphere and suspended in an oil bath at 100 °C for 4 h, with carbonyl concentrations compared before and after testing. These tests showed insignificant differences, demonstrating that the tribometer test procedures themselves would not significantly further degrade the oil samples, thereby changing the properties of the oil during the test period. Although some interfacial heating could occur during testing resulting in localized thermal degradation, this would involve a very small quantity of oil in comparison to the bulk oil. However re-running the FTIR analysis at the end of the tests was not possible due to the quantities of oil needed for this and the GC analysis, required to be able to correct for the volatile content of each sample.

### 3.6 Rheological analysis

The dynamic viscosity of the oil samples was determined using a Bholin CV120HR rheometer at 40 and 100 °C. The measurements were made using a 40 mm diameter cone on plate with a 100  $\mu\text{m}$  gap and the average of five measurements recorded.

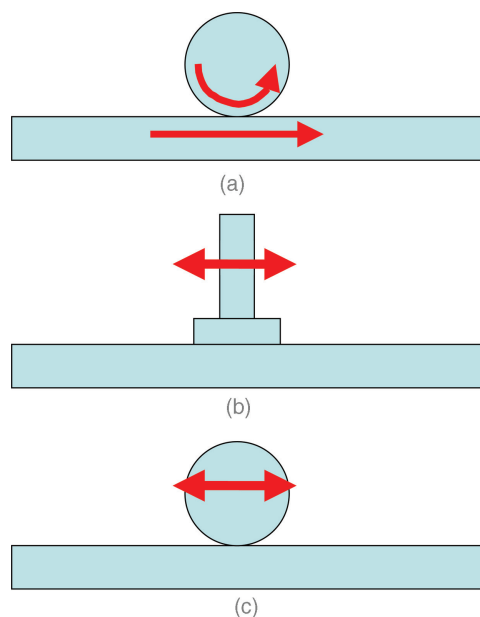
### 3.7 Tribological tests

Three sets of tribological tests were undertaken each representing a different contact geometry. These

included the use of a mini traction machine (MTM), high frequency reciprocating rig (HFRR) and a Plint high speed short stroke friction rig (TE-77). The aim of these preliminary tests was to begin to investigate how the TRZ samples affected traction coefficients and wear in comparison to the fresh oil and used sump oil. Because of the small quantities of oil available for these tests, a number of adaptations were made to the MTM and the TE-77 as described in sections 3.7.1 and 3.7.2. In all the tribological tests, a temperature of 100 °C was used as this is the top ring reversal liner temperature for this engine at 1500 r/min, 50 per cent load. At 33 and 75 per cent load, the liner temperatures are 98 and 101 °C, respectively. TRZ temperatures have yet to be measured for this engine.

#### 3.7.1 Mini traction machine

An MTM (PCS Instruments, London, UK) was employed to characterize the properties of the lubricant samples in a mixed sliding/rolling contact regime (Fig. 3(a)). All the friction measurements were performed under a fixed contact pressure of 1 GPa and 50 per cent slide roll ratio (SRR) with the first run undertaken at 80 °C and then immediately repeated at 100 °C. All subsequent runs were undertaken at 100 °C consecutively after time periods of 5, 5, 10, and 15 min. During each run, the speed was altered from 3.5 to 0 m/s in 32 equal steps and the



**Fig. 3** Schematics of tribometer contact geometries (a) MTM – rolling/sliding; (b) TE-77 – pure sliding, and (c) HFRR – simple sliding

traction coefficients recorded. At the end of the test, a final set of measurements was taken at fixed speed with the SRR varied between 0 and 100 per cent in 5 per cent steps. This test sequence was repeated for each oil sample and one set of ball and disc was used for each lubricant sample. The ball and disc samples were manufactured from AISI 52100 bearing steel and finished to  $0.01\ \mu\text{m}$  Ra with hardness 729–739 and 688–722 BHN, respectively. To investigate the difference in lubricant behaviour at different speeds, the coefficient of friction versus mean velocity plots at 50 per cent SRR were obtained. On the MTM, the traction coefficient ( $dF/dN$ ) is measured as a function of mean velocity.

A horseshoe adapter was manufactured from stainless steel so that it sat within the oil sample bowl of the MTM (Fig. 4), thereby reducing the oil quantity required to 5 ml for the test while still allowing the oil thermometer to remain in contact with the oil sample. This adaption was shown not to affect the operation of the MTM by comparing repeated runs with the fresh and sump oil samples.

### 3.7.2 *Plint high speed short stroke friction tribometer (TE-77)*

The TE-77 (Phoenix Tribology Limited, Newbury, UK) was employed as a pin-on-plate tribometer (Fig. 3(b)) to characterize the friction and lubricant properties of the lubricant samples in the pure sliding contact regime. In this set-up, a 5 mm diameter pin finished to  $0.05\ \mu\text{m}$  Ra to represent the face of a piston ring was reciprocated against a plate ground to  $0.4\ \mu\text{m}$  Ra at  $45^\circ$  to the direction of stroke in order to represent the surface finish of a cylinder liner. Both the plate and the pin samples were manufactured from the Hydra engine grey cast iron liner with hardness 230–300 BHN.

The stroke was set to 5 mm, the frequency to 25 Hz (representing 1500 r/min), and the pin loaded with 5 kg, giving a contact pressure in the region of 2.6 MPa. This contact pressure represents the maximum nominal radial applied pressure experienced

by the ring–liner contact in the Hydra engine just after combustion at 50 per cent of maximum engine load.

During these tests, the friction coefficient was measured by a piezo cell and the average metallic contact measured by passing 50 mV across the pin and plate. To investigate the difference in the lubricants, both friction coefficient and the average metallic contact were logged per half reciprocation and recorded as an average every 3 min using a PC and the National Instruments LabView program.

The sump of the TE-77 was modified so that its internal capacity was considerably smaller than the standard sump and this allowed a 2 ml lubricant sample to be placed in the sump and cover the test samples for the duration of the test.

### 3.7.3 *High frequency reciprocating rig*

The HFRR (PCS Instruments, London, UK) was employed as a ball-on-flat tribometer (Fig. 3(c)) to characterize the friction and lubricant properties of the lubricant samples in the simple sliding contact regime. In this test, a 6 mm diameter ball was moved back and forth over a 10 mm diameter disc at 20 Hz (representative of 1200 r/min) with 1 mm stroke length. A load of 400 g was placed on the ball giving a maximum Hertzian contact pressure of 1 GPa. The ball and flat were manufactured from AISI 52100 bearing steel and finished to 0.05 and  $0.02\ \mu\text{m}$  Ra, respectively, both with hardness 615–740 BHN. The test was started at  $40^\circ\text{C}$  and increased to  $140^\circ\text{C}$  in  $20^\circ\text{C}$  steps. Each temperature was run for 5 min and then halted to allow for the  $20^\circ\text{C}$  temperature rise where the oil was allowed to equilibrate for 1 min before starting the next run. The HFRR uses a strain gauge to measure the friction and the average of this over the 5 min run at each temperature was logged for each lubricant. The HFRR test can be performed with less than 3 ml of oil and, as such, no alterations were required to this test apparatus.

## 4 RESULTS

Selected results are presented as full results and discussion of each test are beyond the scope of this paper.

### 4.1 Chemical analysis

Figure 5 shows the FIMS results and displays the abundance of non-cyclic alkanes (with a size range of ca 15–40 carbons) and of alkyl benzenes (size range of ca 6–15 carbons) in the base fluid. The fresh oil and sump oil that has not passed through

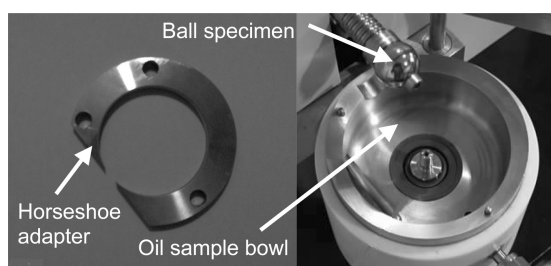


Fig. 4 MTM horseshoe adapter



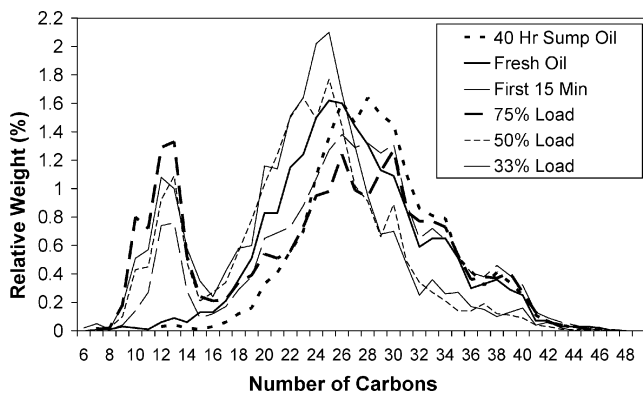


Fig. 5 FIMS results showing relative abundance of non-cyclic alkanes and alkyl benzenes of different sizes in the oil samples

the TRZ do not have alkyl benzenes present in significant quantities.

Figure 6 presents the volatile content of the six oil samples as defined by GC. The fresh oil has no measurable volatiles, the sump oil has the least volatile content, and the first 15 min from cold start contains the maximum level of volatiles.

Figure 7 shows the carbonyl concentrations present in the six oil samples as defined by FTIR spectroscopy. It can be seen that the TRZ carbonyl concentrations are considerably higher than that of the sump oil. The fresh oil exhibits a zero value for carbonyl concentration due to degradation, as would be expected.

### 4.2 Rheological analysis

Figure 8 presents the viscosity results obtained for the six oil samples at 40 and 100 °C. All tribological tests were undertaken at 100 °C and it can be seen that there are distinct differences in viscosity values between the oils that have passed through the TRZ

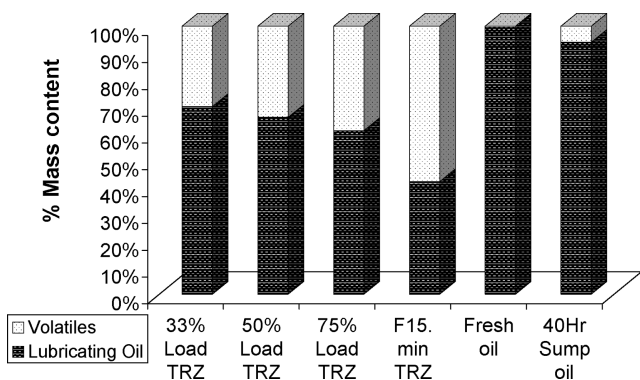


Fig. 6 Lubricant samples volatile content as defined by GC analysis

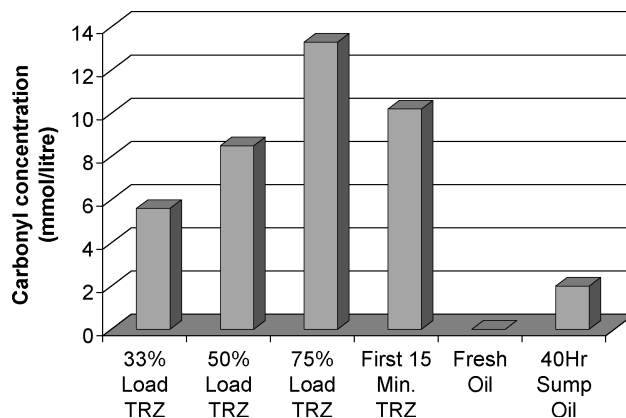


Fig. 7 Comparison of carbonyl concentrations for the six oils tested using FTIR spectroscopy

and the fresh and used sump oils. There is little difference in the first 15 min sample at 40 and 100 °C. The five results obtained at 100 °C for the first 15 min sample, from which the plotted value is an average, showed a steep climb in viscosity at the start of the test.

### 4.3 Tribological analysis

#### 4.3.1 Mini traction machine

Figures 9 and 10 show the traction coefficient values for the oil samples with respect to log sliding speed at 100 °C and 50 per cent SRR. It can be seen that the 40 h used sump oil sample has noticeably higher traction coefficients than the other five oil samples. The values shown in Fig. 9 are for the first readings taken at 100 °C, and the values shown in Fig. 10 are for the fifth readings taken at 100 °C. It can also be seen that the fresh oil and used sump oil do not level off at slower speeds in Fig. 9 as the TRZ oil

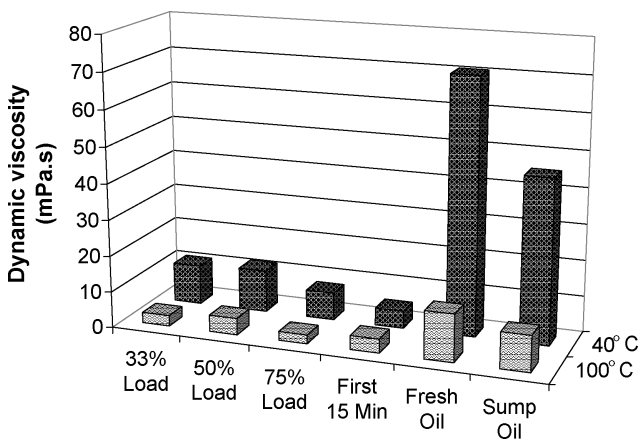
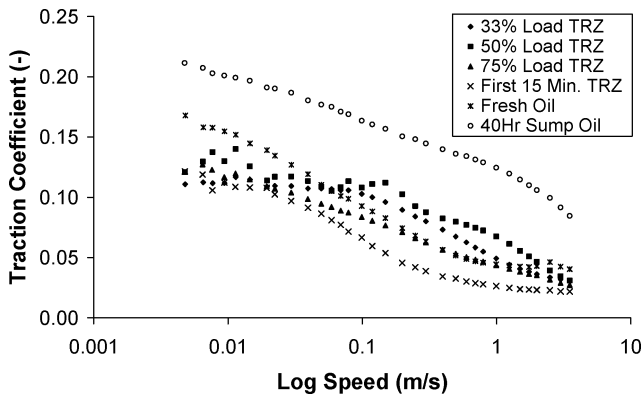


Fig. 8 Viscosity values (Pa. s × 10<sup>-2</sup>) at 40 and 100 °C for oil samples





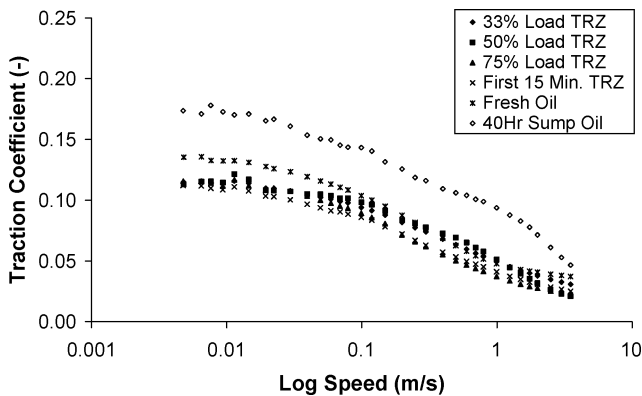
**Fig. 9** MTM traction coefficient values for the oil samples with respect to log sliding speed at 100 °C, 50 per cent SRR (first run)

traces do, but continue to increase in traction coefficient value.

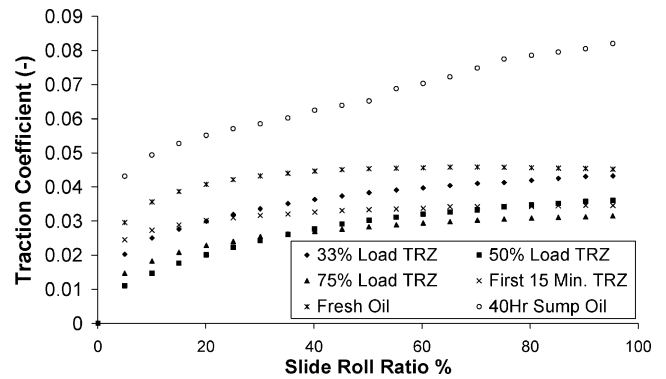
Figure 11 presents the traction coefficients values for changing SRRs at constant speed, again it can be seen that the 40 h used sump oil sample returns higher values and a different trend. These results were obtained at the end of each oil sample test after one set of readings had been taken at 80 °C and five sets of readings had been taken at 100 °C.

**4.3.2** *Plint high speed short stroke friction tribometer*

Figure 12 shows the friction coefficient values for the TE-77 and it can be seen that the TRZ samples show a trend of lowering with respect to time, whereas the fresh oil and sump oil sample follow the trend of remaining relatively constant. The average metallic contact results showed no obviously discernable pattern other than to confirm boundary lubrication and have therefore not been presented.



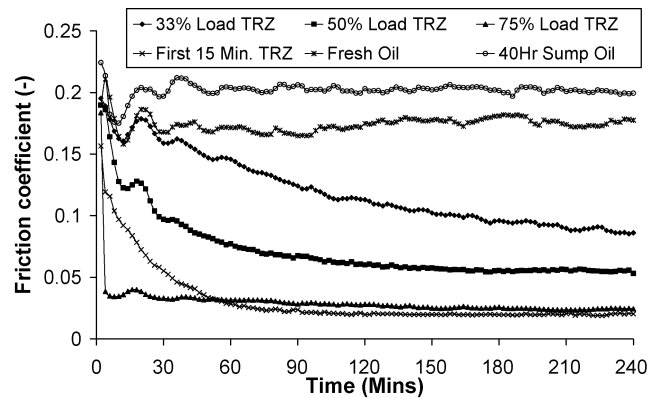
**Fig. 10** MTM traction coefficient values for the oil samples with respect to log sliding speed at 100 °C, 50 per cent SRR (fifth run)



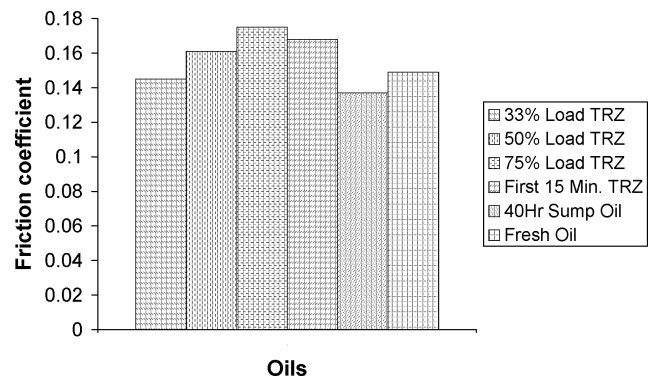
**Fig. 11** MTM traction coefficient values for the oil samples with respect to SRR at constant speed

**4.3.3** *High frequency reciprocating rig*

Table 1 presents the full results obtained for the oil samples using the HFRR. These show that there are no significant differences between the results; however, there are general trends that follow the level of engine load for the TRZ samples at 100 °C as shown in Fig. 13.



**Fig. 12** Friction coefficient values obtained from the TE-77 for the six oil samples with respect to time



**Fig. 13** HFRR friction coefficient values at 100 °C for the six oil samples

## 5 DISCUSSION

The extraction of the TRZ samples over a relatively short engine operating period of 40 h makes it highly likely that the oil will have only passed through the TRZ once or twice prior to extraction. It should be noted that in an operating engine towards the end of the drain interval the oil may have passed through the TRZ in excess of ten times [7]. Previous work [1] has shown that the fully formulated oil used in these tests has an induction period prior to beginning to degrade. This induction period corresponds to the length of time it takes for the additives to be consumed as they prevent the oil degrading. The results presented here are, therefore, for lightly degraded TRZ samples and not for highly degraded TRZ samples as would be present in an engine prior to a scheduled oil change.

### 5.1 Chemical

The FIMS results (Fig. 5), shows alkyl benzenes (ca 6–15 carbons) are present in the TRZ samples, with insignificant amounts in the fresh oil and sump oil samples. These volatiles are caused by the lighter mass base oil compounds, the quenching of the combustion process on the liner wall being representative of soot precursors as well as the heavier mass fuel volatiles. Most of the lighter mass fuel volatiles are likely to have remained in the gas phase when the TRZ samples were condensed on the sample vial wall and will have been lost to the gas extraction system. The progressive increase of alkyl benzenes with engine load concurs with this argument when it is considered that the engine load was increased by the addition of fuel to the combustion process. This will have resulted in higher levels of unburnt fuel in the TRZ as well as a hotter flame being quenched on the liner. Between 33 and 75 per cent load, the liner temperature at top ring reversal only increases by 3°, from 98° to 101°, and therefore liner temperature will have had little effect on the levels of quenching. The largest increase in temperature due to the increased load will have been in the ring pack, from where the degraded samples were collected.

The first 15 min sample contains high levels of volatiles as the engine would have been cold and this will have allowed higher levels of quenching of the combustion process on the liner. This will, in theory, have resulted in higher levels of volatiles as will the lower engine temperature resulting in less evaporation of volatile compounds. However, the oil will also have been colder, and therefore more viscous, resulting in higher quantities of oil in the ring pack. The increased tolerances between rings, liner,

and piston due to the components being cold will also have enabled higher levels of oil to be present in the ring pack. These higher levels of oil will have increased the levels of base oil carbons (non-cyclic alkanes (ca 15–40 carbons)) in the ring pack and therefore affected the proportion of non-cyclic alkanes to alkyl benzenes such that the volatile peak for FIMS analysis has become lower than that for the 75 per cent load TRZ sample.

The same pattern for volatile content is observed for the GC-FID analysis (Fig. 6), with the exception of the first 15 min sample. This may be due to the different analysis technique detecting a wider range of volatile compounds. The limited quantities of TRZ sample available meant that it was not possible to repeat the FIMS and GC-FID analysis to investigate this further.

Because of using fully formulated oil, it cannot be assumed that all the oxidation detected in the carbonyl region by the FTIR analysis has been caused by base fluid oxidation (Fig. 7). Other factors will include the dilution of carbonyl-containing additives (such as succinimides) both while running in the engine and during analysis. This can make the use of carbonyl concentration, as a means of measuring lubricant degradation of fully formulated oil, difficult to interpret.

However, despite these issues, patterns can be seen, which fit with the theory and results found in previous works [1, 6, 7]. The carbonyl content in the TRZ samples increases with engine load and is significantly higher than that seen in the sump oil and fresh oil. Additionally, the first 15 min sample is returning a value between the 33 and 75 per cent TRZ samples, which is consistent with the pattern seen in the tribological, FIMS, and rheological results, and is likely to be due to the proportion of alkyl benzenes to non-cyclic alkanes as discussed for the FIMS result.

Repeating this work with an oil blend of hydrocarbon base fluid, 2 per cent w/w sulphonate detergent and 2 per cent w/w succinimide dispersant will allow easier chemical analysis. This oil blend has successfully been used for chemical analysis in previous work [1].

### 5.2 Rheological

In general, it can be seen that the level of volatiles in the TRZ samples has a direct impact on the viscosity of the lubricant; the higher the volatile content, the lower the viscosity. This is particularly obvious when comparing the sump oil and fresh oil, which have minimal volatile content, with the TRZ samples. The reason for the 50 per cent load TRZ sample not fitting this pattern may be due to experimental

error or engine phenomena. Unfortunately, due to the quantity of oil available, it was not possible to repeat the viscosity measurements with the TRZ samples; however, repeats with the fresh and sump oils indicated repeatability of  $\pm 0.3$  per cent.

The similarity of the viscosity value for the first 15 min sample at 100 and 40 °C is likely to be due to the evaporation of higher end volatiles at 100 °C. The observation during testing of a dramatic rise in viscosity once the 100 °C test began supports this theory. This phenomenon is far more likely to occur with the first 15 min TRZ sample than the other TRZ samples due to the excessive amount of fuel required to choke the engine when it is cold in order for it to run. This results in unburnt fuel mixing with the oil and travelling down the sample pipe as liquid mixed with the oil into the sample vial. There is also likely to be higher quantities of water present in the first 15 min sample due to the quenching of the combustion products on a significantly colder liner than when the engine has reached thermal equilibrium.

### 5.3 Tribological

#### 5.3.1 Mini traction machine

It should be noted that the right-hand side of Figs 9 and 10 are the speeds at which engine components are most likely to operate. Although the piston ring and liner contact will become stationary, as signified by the left-hand side of the graphs, this happens very quickly and only momentarily, representing a very small proportion of the overall cycle. Figure 9 shows the first results obtained at 100 °C and Fig. 10 shows the final result at 100 °C after rolling sliding contact for over 1 h. It can be seen that there is a reduction in traction coefficient for the fresh oil and the 40 h sump oil and that the TRZ oils become more clustered. These observations are likely to be due to the effect of surface film formation as the surfaces interact. Although the traction coefficient values for the sump oil are significantly higher throughout the first 100 °C run (Fig. 9), these become lower during the final 100 °C run (Fig. 10) and there is little difference between all the samples

at typical engine speeds of above 3 m/s. It is also noteworthy that there are different traction coefficient curves for the TRZ oils to those for the 40 h sump and fresh oils in Fig. 9 with the TRZ oils leveling off at slower speed and the 40 h sump and fresh oils continuing to rise. This difference is less obvious in Fig. 10 and shows further effects of film formation. Fresh (green) oil does not provide full engine protection as the oil has to be 'broken in'. Many of the additives do not start to fully interact with each other until they begin to break down in the engine at the temperatures at which they are designed to work. It is therefore possible that the fresh oil, which has not been exposed to engine operating conditions, provides a reduced level of protection compared with the sump oil that has been run in the engine. The TRZ sampled oils provide reduced levels of protection due to their degradation in the ring pack. As such, the fresh oil and TRZ oils return similar levels of protection, but for different reasons. Further research will be required to confirm this.

Surface analysis techniques would be required to confirm this theory and investigate the types of films formed and any differences between the samples.

Little can be concluded from the order of the TRZ samples as they are essentially the same when repeatability of  $\pm 0.01$  friction coefficient is considered. This value was found by repeating the procedure with sump and fresh oil samples.

The results for change in SRR, shown in Fig. 11, were taken after the film had been formed, and it can be seen that the fresh oil behaves in a similar manner to the TRZ oils as the traction coefficient values level out after 40 per cent SRR. However, the traction coefficient values continue to rise throughout this test for the 40 h sump oil sample.

#### 5.3.2 (TE-77) Plint high speed short stroke friction tribometer

The decrease in friction coefficient values at the start of the tests for each different per cent load oil corresponds to the levels of volatile content, with higher volatile content oils displaying greater reductions in friction coefficient than lower volatile content oils (Table 2). This will be due to the evaporation of the

**Table 2** Friction coefficient values and wear scar measurements at six temperatures for the six oil samples **Q3**

Oil Sample	$\mu$ -value for different temperatures (°C)					
	40	60	80	100	120	140
33% load TRZ	0.132	0.132	0.143	0.145	0.146	0.144
50% load TRZ	0.130	0.149	0.168	0.161	0.155	0.152
75% load TRZ	0.143	0.157	0.172	0.175	0.171	0.166
First 15 min	0.150	0.164	0.168	0.168	0.164	0.153
Fresh oil	0.124	0.129	0.137	0.149	0.150	0.150
40 hr Sump oil	0.129	0.131	0.133	0.137	0.144	0.147

volatiles during the test. Samples with higher volatile content took longer for the oil to reach a constant friction coefficient value than those with lower volatile content. This supports the theory that lighter volatiles are created by lower quenching temperatures, as these lighter volatiles are more prone to evaporation at temperature. The first 15 min sample presents between the 33 and 75 per cent load TRZ samples and has a steadier curve. This may be the effect of water evaporation, which will be slower than volatile evaporation.

The levels of friction coefficient follow the same trend as the engine load with higher friction coefficients being presented by the lower load TRZ samples. This combined with the lower friction coefficients presented by the TRZ samples over the fresh and sump oils suggests that degraded TRZ samples offer higher levels of protection against component wear than fresh or sump oil in this test. There may also be the effect of film formation over time; however, there appears to be little change in friction coefficient with respect to time for the fresh or sump oil.

### 5.3.3 High frequency reciprocating rig

In this test, the fresh oil and sump oil have returned lower friction coefficient values than in the MTM and TE-77 test. This is likely to be due to the test procedure contact geometry of a sliding ball on plate where film formation and collapse are slow. The 33, 50, and 75 per cent load TRZ sample friction coefficient values follow the same pattern as the load values, with higher traction coefficients for higher loads. This is the opposite result to those obtained from the pure sliding contact geometry of a pin-on-plate in the TE-77 test where film formation and collapse are faster, thereby providing more protection. The first 15 min TRZ sample is between the 33 and 75 per cent load values as seen in the TE-77, FIMS, and rheological results. Further research would be required to elucidate the reasons for the difference in results between the HFRR and TE-77.

## 6 CONCLUSIONS

1. A sampling system has been successfully used to extract relatively large (25 ml) quantities of oil from the rear of the top piston ring of an operating gasoline engine. This is the first time such large quantities of oil have been sampled from the TRZ of a gasoline engine and such extensive chemical and rheological analysis undertaken.
2. The samples collected have undergone a comprehensive range of chemical, rheological, and tribological analysis. Distinct differences have been observed between the TRZ samples and the fresh

and sump oil samples. Correlations between the TRZ oils with respect to the engine load at which they were sampled have also been observed.

3. The results have shown that the sump oil is not comparable to TRZ oil and, therefore, not suitable oil to use to further elucidate component interaction at the piston ring/liner interface.
4. This paper provides a basis to further develop the sampling and analysis of TRZ samples.

## ACKNOWLEDGEMENTS

Thanks are extended to Shell Global Solutions (UK) for their financial support and undertaking the FIMS analysis and Infineum UK Ltd for undertaking the HFRR experiments. The authors would like to thank the Mechanical Engineering Department, Imperial College London for the use of an MTM.

## REFERENCES

- 1 Lee, P. M. *et al.* The degradation of lubricants in gasoline engines: development of a test procedure to evaluate engine oil degradation and its consequences for rheology. In 31st Leeds-Lyon Symposium. **Q4**
- 2 Korcek, S. and Jensen, R. K. Relation between base oils composition and oxidation stability at increased temperatures. *ASLE Trans.*, 1976, **19**(2), 83–94.
- 3 Korcek, S. and Johnson, M. D. Effect of NO<sub>x</sub> on liquid phase oxidation and inhibition. In *Engine oils and automotive lubrication* (Ed. Bartz, W. J.) 1993, pp. 177–199 (Marcel Dekker, Inc., New York).
- 4 Yatsutomi, S., Maeda, Y. and Maeda, T. Kinetic approach to engine oil: 1—analysis of lubricant transport and degradation in engine system. *Ind. Eng. Chem. Prod. Res. Dev.*, 1981, **20**, 530.
- 5 Korcek, S. and Maloney, L. R. *Mechanisms of antioxidant decay in gasoline engines: investigations of zinc dialkyldithiophosphate additives*. SAE paper 810014, 1981.
- 6 Stark, M. S. *et al.* The degradation of lubricants in gasoline engines: lubricant flow and degradation in the piston assembly. In 31st Leeds-Lyon. *Life cycle tribology*, Leeds, UK, 2004. **Q4. Q5**
- 7 Stark, M. S. *et al.* Measurement of lubricant flow in a gasoline engine. *Tribol. Lett.*, 2005, **19**(3), 163–168. **Q4**
- 8 Taylor, R. I. and Evans, P. G. *In-situ* piston measurements. *Proc. Instn Mech. Engrs, Part J: J. Engineering Tribology*, 2004, **218**, 185–200.
- 9 Saville, S. B. *et al.* SAE technical paper 881586. International Fuels and Lubricants Meeting, 10–13 October 1988. **Q4. Q5**
- 10 Emanuel, N. M., Denisov, E. T., and Maizus, Z. K. *Liquid phase oxidation of hydrocarbons*, 1997 (Plenum Press, New York).
- 11 Dong, J., Van-de-Voort, F. R., and Ismail, I. I. Rapid determination of carboxylic acid contribution to the total acid number of lubricants by FT-IR. *Lubri. Eng.*, 2000, **12**. **Q6**

