

promoting access to White Rose research papers



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

White Rose Research Online URL for this paper:
<http://eprints.whiterose.ac.uk/4875/>

Conference paper

Lee, P.M. (2008) *Tribological investigations of the piston assembly and liner of a gasoline engine*. In: Inaugural Automotive Researchers Conference, 8-9 January 2008, Huddersfield University.

Tribological Investigations of the Piston Assembly and Liner of a Gasoline Engine

Peter M Lee

iETSI, School of Mechanical Engineering, University of Leeds, Leeds. LS2 9JT

ABSTRACT

The automotive industry is being forced towards greater efficiency, increased engine power from smaller engines and lower environmental impact by both governmental legislation and public opinion. Oil drain intervals are increasing whilst emissions legislation limit the use of current wear protection and antioxidant additives containing elements such as phosphorus and sulphur. To address these demands and challenges an increased understanding of the link between lubricant degradation, its transport and residence time, and the effect on piston assembly tribology is required.

The aim of the work reported in this paper was to further develop the understanding of the effect degraded lubricants have on piston assembly tribology. The small oil volumes and environmental conditions in the piston assembly make the affective lubrication and protection of components in this region one of the most challenging areas of tribology. This was carried out through an extensive experimental programme using a research engine, tribometer testing and chemical and rheological analysis of lubricant samples.

Keywords: Engine tribology, Piston assembly, Oil sampling

INTRODUCTION

It is generally accepted that conventionally fuelled vehicles will dominate the automotive market for the foreseeable future and alternative fuels, such as fuel cells and hydrogen, will present a slow penetration into this market [1]. Even with the projected rise in the use of crude oil there is currently a minimum of 40 years in reserve and the total proven world oil reserves have remained constant for the 12 years to 2001 due to the discovery of new oil fields and increased use and development of technology to extract these reserves [2]. Conventional oils will therefore continue to dominate as both lubricants and fuels for a long time to come and, on the surface, little will change in the lubrication of the internal combustion engine. However, below the surface much is changing.

The automotive industry is being forced towards greater efficiency (resource utilisation), increased engine power and lower environmental impact by a combination of governmental legislation and public opinion. OEMs are steadily increasing oil drain intervals requiring that the oil withstand the degradation processes experienced in an engine for longer periods of time.

At the same time as lubricant manufacturers are undertaking the challenge of lowering phosphorus levels, vehicle body design changes are being made to reduce drag to increasing fuel efficiency. These design changes are resulting in less air flow through the engine bay, and therefore further increases in the operating temperature of the lubricating oil, which in turn increases the rate of thermal degradation in the ring pack. Operating conditions of the lubricant in the engine are also becoming increasingly harsh with the continuing trend to develop engines with higher power densities, which again results in higher operating temperatures. Demands placed upon engine lubricating oils will continue to increase in the future as engine designers use new developments such as EGR to lower combustion temperatures, injection profiling to obtain homogeneous burns, turbo-charging, changing of compression ratios and as yet undeveloped and undiscovered technology.

The interaction between the piston assembly and the liner in an engine accounts for between 40% to 60% of mechanical losses in the engine dependant upon operating conditions. The level of mechanical loss is directly related to the tribological interaction between the piston assembly and the liner and it is therefore essential that this is understood in order to reduce these losses. However it is difficult to elucidate information from this region due to its enclosed, high pressure and chemically hostile nature.

The effect of the environment in which the ring pack and liner operates is such that the lubricant becomes thermally degraded in this region and then flows back down to the sump where it mixes with the fresh sump oil. This has been shown by many researchers after it was first proposed by Yatsutomi [3]. It therefore follows that the oil in the ring pack and liner region is not the same as the oil in the sump and, as such, samples of this oil are required in order to elucidate the tribological interactions in this region.

The specific aim of this research was to begin to look at how the degraded oil in the top ring zone affected the tribological performance of the ring pack. This was achieved through a novel and comprehensive chemical, rheological and tribological assessment of the oil extracted from the ring pack of the engine under a range of engine loads.

EXPERIMENT

To enable the study of how oil in the top ring zone (TRZ) of a fired engine affects the tribological performance of the ring pack it was necessary to extract oil from this region and a TRZ sampling system was developed. Relatively large samples of oil were collected (25ml) at different loads from the TRZ over prolonged engine runs (40hrs), and these oil samples, along with both fresh and used sump oil, were subjected to a series of tests including wear Plint TE-77 reciprocating tribometer, PCS mini traction machine (MTM), high frequency reciprocating rig (HFRR) tribometers and tests for viscosity, fuel and carbonyl content and field ionization mass spectrometry (FIMS). A single cylinder Ricardo Hydra engine was used for this research, as detailed in the Appendix.

TOP RING ZONE (TRZ) SAMPE METHOD

The theory behind the TRZ sampling system is that the differential between the pressure created in the combustion chamber of the engine and atmospheric pressure forces a gas stream through a hole at the back of the top piston ring and down a sample pipe to sample vials. This gas stream entrains oil as a mist and this is then condensed on the vial wall and collected as a sample representative of the oil in the top piston ring zone.

The pipe from the piston to the outside of the engine is in two parts, joined at the big end. The top half is allowed to move freely within a stainless steel sleeve and is fixed to the end cap bolt, Figure 1. The pipe from the crankshaft to the outside of the engine was a more complex problem to solve due to the constantly changing position of the crank in relation to the exit point of the pipe from the engine. The method of Frottier and Heywood [4] was used where the pipe is fed around a single axial constraint, effectively turning it into a coil spring. This prevented it thrashing around uncontrollably and therefore breaking at the unions and clamping points. After rounding all the sharp edges in which the pipe came into contact and adjusting the tightness/length of the pipe, a reliable easily assembled, cheap system was developed, Figure 2.

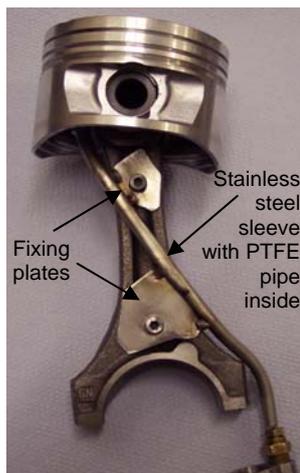


Figure 1: Top half of TRZ sample Pipe

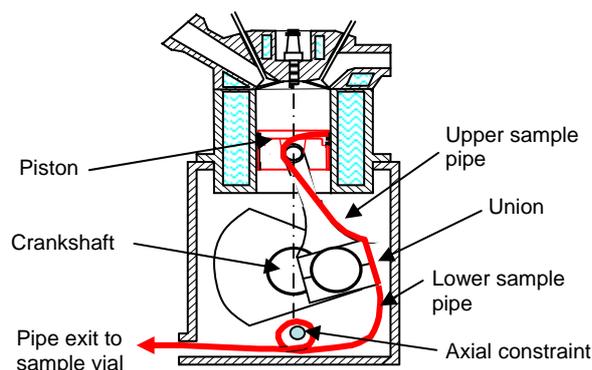


Figure 2: TRZ sample Pipe

Experience from our own work at Leeds and work undertaken both at Shell and De Montfort University [5, 6] have shown that the smallest cross section of the sampling system must be at the sample entrance point in the piston to prevent

deposits blocking the pipe. For this reason a hole size of less than the internal diameter of the pipe was required in the piston.

OIL SAMPLES COLLECTED

The lubricating oil chosen for the test was Shell Helix Super 15w-40. This is a fully formulated Group I base oil that has a lower performance specification additive package and is therefore more prone to degradation than higher specification oils. Three different sets of engine parameters were chosen for this work as shown in Table 1. The six oil sample types to be sampled are defined in Table 2.

Parameter	Units	Tolerance	Set 1	Set 2	Set 3
Speed	rpm	±0.5	1500	1500	1500
Load	Nm / %	±0.5 / 1.4	11.9 / 33	18.0 / 50	27.0 / 75
Throttle	%	±1	50	50	50
AFR	(ratio)	±0.5	16	16	15
Water outlet	°C	-6	80	80	80
Crank oil	°C	±1	63	65	69
Crank sum	litres	±0.05	1.5	1.5	1.5
Test Length	Hours	±0.1	45	45	45

Table 1: Engine Test Parameters

Oil Sample Name	Oil Sample Conditions
33% Load TRZ	Parameter set 1
50% Load TRZ	Parameter set 2
75% Load TRZ	Parameter set 3
First 15 min	First 15 minutes from cold start at 1500rpm
Fresh Oil	Fresh Shell Helix Super 15W-40
40Hr Sump Oil	Parameter set 2 sump oil after 40 hours

Table 2: Conditions of six oil samples collected

When the engine was started from cold at the beginning of each day the ‘first 15 minute TRZ sample’ was collected. This was collected over the first 15 minutes of all the runs regardless of the parameters as when the engine is first started it has to be over-fuelled (choked) in order for it to run and therefore there was no difference in the load during this period. Once the first 15 minute sample had been collected the crank block heaters were turned on to help the engine reach operating temperature. At one hour from start-up, with the engine parameters set as required and the block heaters turned off, TRZ samples were collected for the remainder of the run (8 hours). Sample collection was stopped just before shut down to ensure that no excess fuel or poor combustion products were inadvertently sampled.

CHEMICAL ANALYSIS

The range of chemical analyses was chosen based upon a desire to investigate the levels of volatiles in the samples, indication of any changes in molecular weight and the levels of degradation that had occurred. The specific methods chosen were influenced by those offered by the overall project collaborators; Shell Global Solutions, Infineum and the Chemistry Department at York University.

Field Ionisation-Mass Spectroscopy (FIMS)

Field ionisation mass spectrometry (FIMS) is an invaluable technique for analysing complex mixtures, particularly fossil fuels. The vaporised oil sample is passed through a very strong electric field which polarises the molecules and guides

them to regions of greater field strength, ultimately resulting in their ionisation. Mass spectroscopy can then be performed on these ionised molecules using conventional magnetic sector or quadrupole techniques. FIMS gives a reasonably accurate molecular weight profile and the profile obtained is not complicated by the size, shape, or functional groups of the molecule, nor is it affected by hydrogen-bonds.

Gas Chromatography (GC)

Gas Chromatography (GC) is essentially a separation method dependent on the differences in boiling point of the components of the sample. A carrier gas (He or N₂) carries the sample as a solute through a separation column and into a detector. The detector is a heated element and as the gas flows through the detector the heat from the element is carried away by the gas. Light gasses such as He and N₂ have high thermal conductivity and any solute in the gas will decrease its conductivity allowing the element to heat up and its resistance change. This change in resistance is converted to a voltage and plotted as a function of time, resulting in a chromatogram. This method is particularly suitable for this work as it can be undertaken with as little as 10⁻³ ml and has detection limits in the low picogram or femtogram range. A marker was added to the lubricant sample and then analysed using a Zebron ZB-5 column.

A GC fitted with a flame ionisation detector (FID) was used to analyse the quantity of volatiles present in the lubricant samples. The Flame Ionization Detector is the most commonly used GC detector, responding linearly from its minimum detectable quantity of about 100 picograms to almost 100%. The FID responds to any molecule with a carbon-hydrogen bond. The FID response is very stable from day to day, and is not susceptible to contamination from dirty samples.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy was used to identify the carbonyl species that are formed during hydrocarbon oxidation [7]; these have been recognised as a good indicator for determining the extent of oxidation in an oil sample as they are representative of the level of hydrocarbon base oil degradation [8-11]. Within this IR spectra, ketones, carboxylic acids and aldehydes can be identified as they are formed by a reaction with oxygen and form carbon-oxygen double bonds. These double bonds are detected by the IR spectroscopy technique, which uses the principle that each different type of bond has a unique frequency and hence energy of vibration [12]. Quantification of the IR spectra was achieved by comparison of the peak area to that of known standard solutions.

RHEOLOGICAL ANALYSIS

The dynamic viscosity of the oil samples was determined using a Bohlin CV120HR rheometer at 40°C and 100°C. The measurements were made using 40mm diameter cone on plate with a 100 micron gap and the average of five measurements recorded.

TRIBOLOGICAL TESTING

Three types of tribological test were undertaken each representing a different contact geometry. These included the use of a Mini Traction Machine (MTM), Plint high-speed short-stroke friction rig (TE-77) and a High Frequency Reciprocating Rigg (HFRR). The aim of these preliminary tests was to investigate how the TRZ samples affected traction coefficients and wear in comparison to the fresh and used sump oil. Due to the small quantities of oil available for these tests a number of adaptations were made to the MTM and the TE-77. During the tribological tests described in this section the oil samples were tested at 100°C for up to four hours. 100°C was chosen as this is the top ring reversal liner temperature for the Hydra engine at 1500rpm 50% load. At 33% and 75% load the liner temperatures are 98°C and 101°C respectively.

Mini Traction Machine (MTM)

A Mini Traction Machine (MTM, PCS Instruments, London, UK) was employed to characterise the properties of the lubricant samples in a mixed sliding/rolling contact regime, Figure 3a. This was due to the ability of the machine to rotate both the disk and the ball at different speeds. All the friction measurements were performed under a fixed contact

pressure of 1GPa and 50% 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 5min., 5min., 10min. and 15min.. During each test run the rotational speed of the ball and disc was adjusted by the software such that their mean velocity was altered from 3.5m/s to 0m/s in 32 equal steps and the traction coefficients recorded. This test sequence was repeated for each oil sample and one set of ball and disk was used for each oil sample. The ball and disk samples were manufactured from AISI 52100 bearing steel and finished to 0.01µm Ra. with hardness 729-739 BHN and 688-722 BHN respectively. The diameter of the ball was 19 mm (¾ inch) and the radius of the track on the disk was between 20 and 21mm. To investigate the difference in lubricant behaviour at different speeds, the coefficient of friction versus the mean velocity plots at 50% SRR were obtained. On the MTM the traction coefficient (dF/dN) is measured as a function of mean velocity.

In order to allow for the reduced quantity of oil available for the test a horseshoe adapter was manufactured from stainless steel so that it sat within the oil sample bowl of the MTM, Figure 4. This reduced the oil quantity required for the test from 32ml to 5ml while still allowing the oil thermometer to remain in contact with the oil sample.

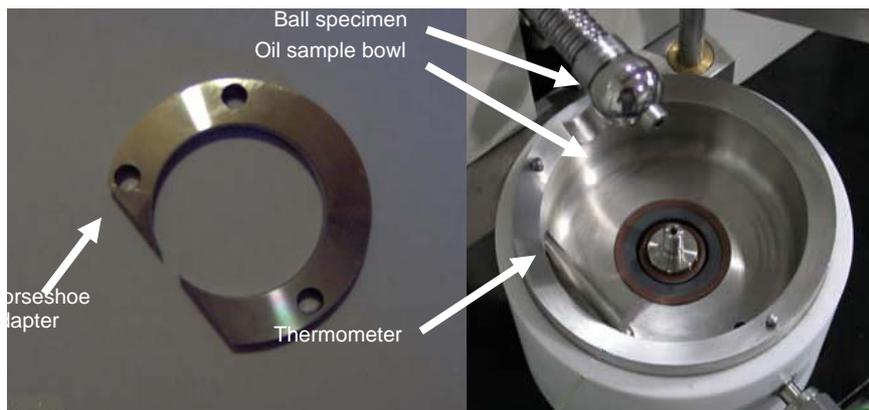
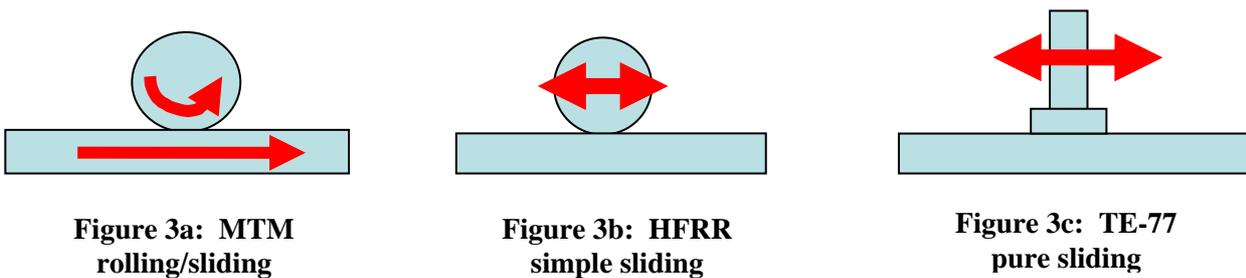


Figure 4: Horseshoe adapter for use with Mini Traction Machine

HFRR

The HFRR (PCS Instruments, London, UK) was employed as a ball-on-disk tribometer to characterise the friction of the lubricant samples in simple sliding, Figure 3b. In this test a 6mm diameter ball was reciprocated over a 10mm diameter disk at 20Hz (representative of 1200rpm in the engine) with 1mm stroke length. A load of 400g was placed on the ball giving a maximum Hertzian contact pressure of 1GPa. The ball and disk were manufactured from AISI 52100 bearing steel and finished to 0.05µm Ra and 0.02µm Ra respectively, both with hardness 615-740 BHN. The test was started at 40°C and increased to 140°C in 20°C steps. Each temperature was run for five minutes and then halted to allow for the 20°C temperature rise where the oil was allowed to equilibrate for one minute before starting the next run. The HFRR test can be performed with less than 3ml of oil and, as such, no alterations were required to this test apparatus to allow for the small quantities of oil available.

Plint High Speed Short Stroke Friction Tribometer (TE-77)

The TE-77 (Phoenix Tribology Ltd., Newbury, UK) is a pin-on-plate tribometer to characterise the friction of the lubricant samples in pure sliding, Figure 3c. In this set up a flat 5mm diameter pin finished to 0.05µm Ra, representing the face of a

piston ring, was reciprocated against a plate ground to $0.4\mu\text{m Ra}$ at 45° to the direction of stroke, in order to represent the surface finish of a cylinder liner, Figure 5. Both the plate and the pin samples were manufactured from the Hydra engine grade 14 grey cast iron liner, with hardness 230-300 BHN.

The stroke was set to 5mm, the frequency to 25Hz (representing 1500rpm in the engine) and the pin loaded prior to testing to 5kg, giving a nominal contact pressure in the region of 2.6MPa. 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% of maximum engine load. The sump of the TE-77 was modified so that its internal capacity was considerably smaller than the standard sump. This allowed a 2ml lubricant sample to be placed in the sump and cover the test samples for the duration of the test as opposed to 15ml.

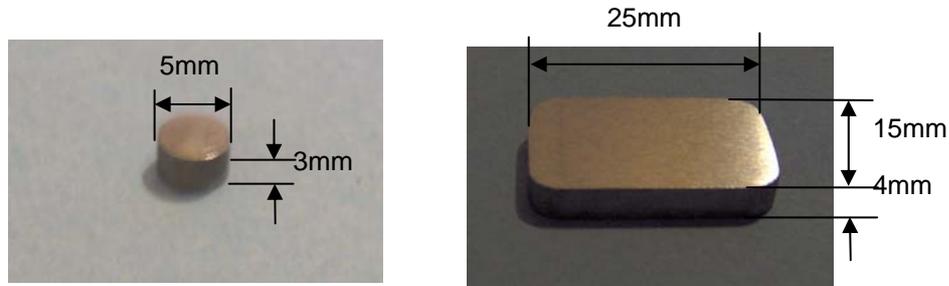


Figure 5: TE-77 pin and plate samples

RESULTS AND DISCUSSION

CHEMICAL RESULTS

The results shown and discussed in this section for the chemical analysis are a summary of the full results obtained due to space limitations.

FIMS

Figure 6 shows a plot of carbon number to relative weight by FIMS for the samples. There is an abundance of non-cyclic alkanes (with a size range of *ca.* 15-40 carbons) in the samples, representing the base fluid. Alkyl benzenes (*ca.* 6-15 carbons) are present in the TRZ samples and are representative of volatiles. These volatiles are caused by the quenching of the combustion process on the liner wall and are 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 therefore 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.

The first 15 minute sample contains a level of volatiles similar to the 50% load sample. These are likely to have been caused by a combination of increased fuelling (chocking) of the engine on start up and a colder liner wall allowing high levels of quenching.

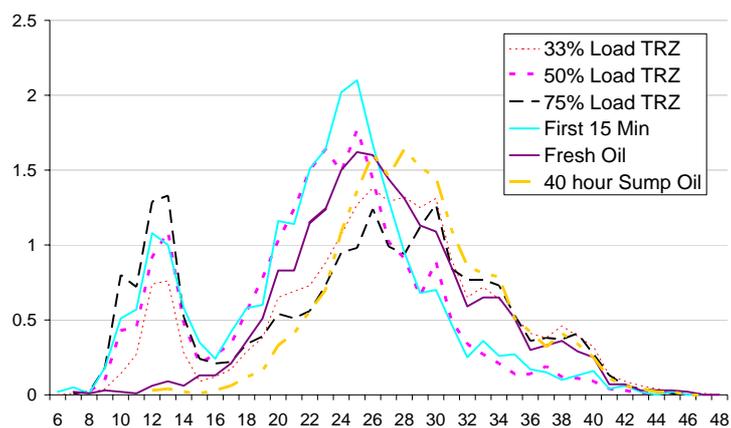


Figure 6: FIMS results showing relative weight of carbon numbers present in the oil samples

GC

Figure 7 presents the volatile content of the six oil samples as defined by GC and shows the same increase in volatile content with engine load as observed by FIMS analysis, Figure 6. The first 15 minute sample displays the maximum level of volatiles by this analysis method. This may be due to the different analysis technique detecting a wider range of volatile compounds or a difference in the time between the samples being removed from the fridge and their ambient conditions during postage to the test sites. The limited quantities of TRZ sample available meant that it was not possible to repeat the FIMS and GC analysis to investigate this further. A 0% volatile content for fresh oil would obviously be the expected result.

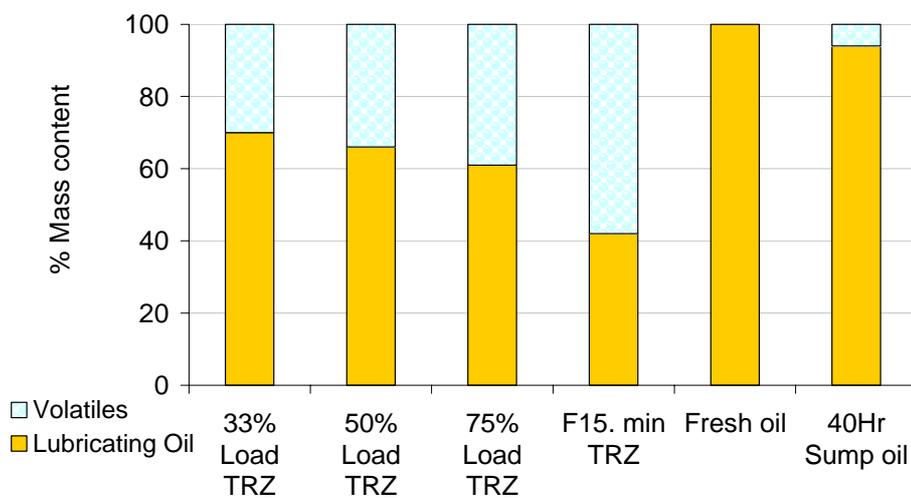


Figure 7: Volatile content as determined by GC analysis

FTIR

Figure 4.15 shows the carbonyl concentrations present in the six oil samples as determined by FTIR spectroscopy. 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. This would be expected as it is the return of these more highly degraded TRZ samples to the sump that causes the majority of the sump degradation.

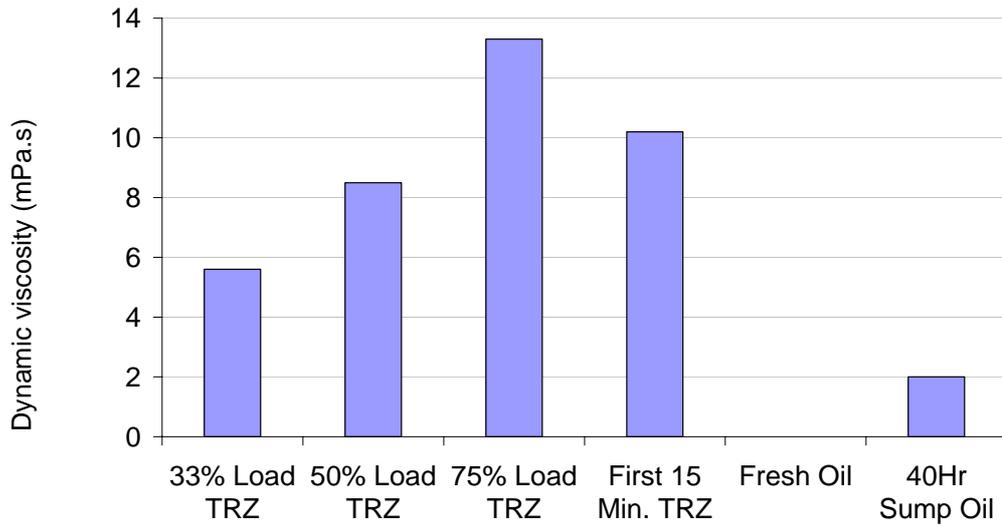


Figure 8: Oil sample carbonyl content by FTIR analysis

RHEOLOGICAL RESULTS

Figure 9 shows the dynamic viscosity of the oil samples at 40°C and 100°C. In general it can be seen that the level of volatiles, Figure 7, in the TRZ samples has a direct impact upon the viscosity of the lubricant; the higher the volatile content the lower the viscosity. This is particularly obvious when comparing the sump and fresh oil, which have minimal volatile content, with the TRZ samples. The 33% load TRZ sample does not fit this pattern, having a lower viscosity than expected when compared with the 50% and 75% values. This may be due to changes in ring dynamics, phenomena of the TRZ sampling system or the higher levels of non-cyclic alkanes in the 15-26 carbon number range, as identified by FIMS, Figure 6. Again due to the quantity of oil available it was not possible to repeat the viscosity measurements with the TRZ samples, repeats with the fresh and sump oil indicated a maximum error of $\pm 0.3\%$.

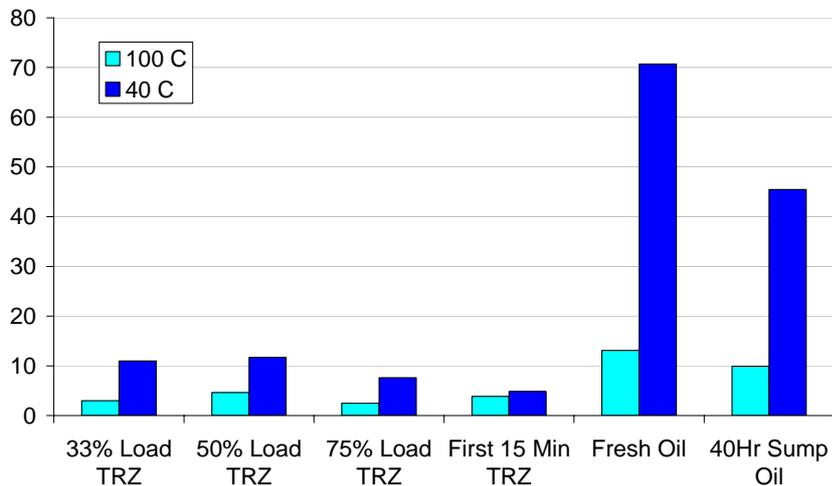


Figure 9: Dynamic viscosity of oil samples at 40°C and 100°C

TRIBOLOGICAL RESULTS

MTM

Figure 10 and 11 show the traction coefficient values for the oil samples with respect to log sliding speed at 100°C and 50% slide roll ratio. It should be noted that the right-hand side of Figures 10 and 11 are the speeds at which engine components are most likely to operate. Although the piston ring and liner contact will become stationary this happens very quickly and only momentarily, representing a very small proportion of the overall cycle. The values shown in Figure 10 are the first readings taken at 100°C and the values shown in Figure 11 are the fifth readings taken at 100°C after rolling sliding contact for over one hour.

There is a reduction in traction coefficient values for the fresh oil and the 40 hour sump oil from the first run to the fifth run and the TRZ oils are more clustered during the fifth run. The traction coefficient values for the sump oil are significantly higher than the TRZ samples during the first run, these become lower during the fifth run. These observations are likely to be due to the effect of surface film formation as the surfaces interact. It is also noteworthy that there are different shapes to the curves with the TRZ curves levelling off at the lower speeds but the fresh and sump oils continuing to rise in traction coefficient value during the first run. This effect is much less obvious during the fifth run and shows further effects of film formation.

There is little difference between the oils at typical engine speeds above 3 m/s and little can be concluded from the order of the TRZ samples as they are essentially the same when repeatability of ± 0.01 traction coefficient is considered. This repeatability value was found by repeating the procedure with fresh and sump oils.

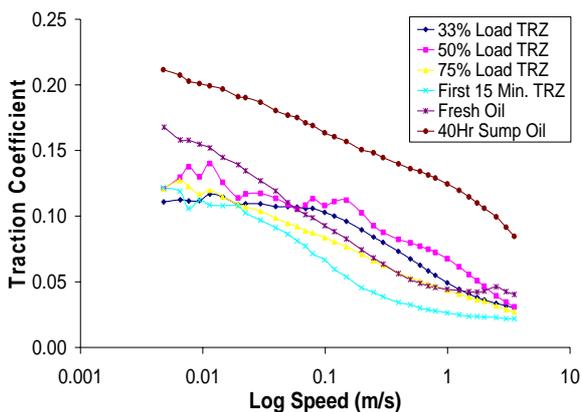


Figure 10: MTM results comparing oil samples for the first test run at 100°C

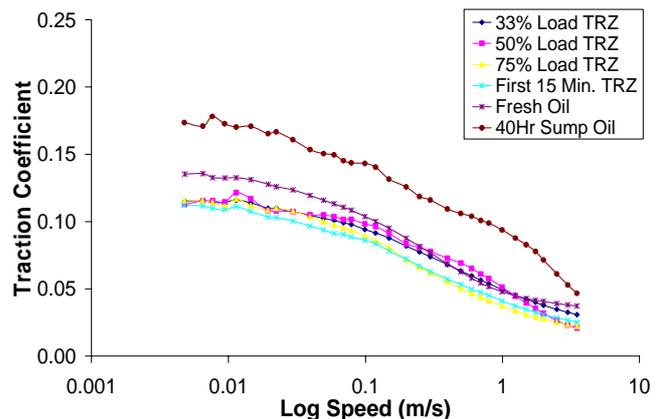


Figure 11: MTM results comparing oil samples for the fifth test run at 100°C

HFRR

Figure 12 shows the friction values obtained at 100°C. Repeatability of ± 0.01 friction coefficient was observed, obtained by repeating the procedure with fresh and sump oils. In this test the fresh oil and sump oil have returned lower friction coefficient values than in the MTM and TE-77 test. These are likely due to the test procedure and the different contact geometry and are values nearer to those of 0.14 that would be expected for engine oils. As the contact geometries for this test are a ball on disk with a contact pressure of 1GPa under simple sliding this results in boundary contact between the components. As such the friction values obtained will be more dependent upon the surface films formed than the viscosity of the oil.

The 33%, 50% and 75% load TRZ sample friction coefficient values follow the same pattern as the load values, with higher friction coefficients for higher loads. This is the opposite result to those obtained from the pure sliding contact experience in the TE-77 test. The first 15min TRZ sample is between the 33% and 75% load values as seen in the TE-77, FIMS and rheological results and likely to be for the same reasons discussed in these sections.

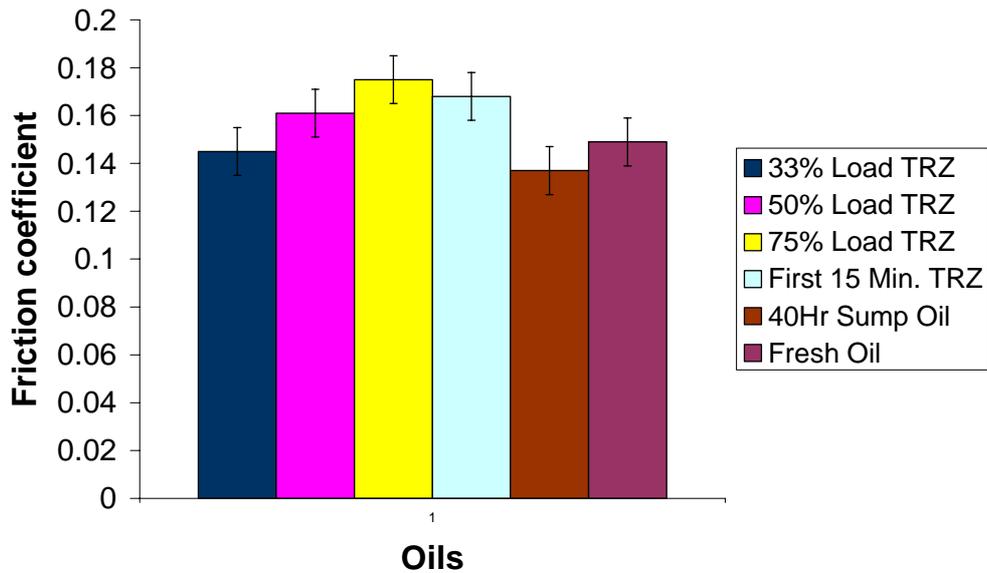


Figure 12: HFRR oil sample friction coefficient values at 100°C errors are ± 0.01

TE-77

Figure 13 shows the friction coefficient values obtained using the TE-77 with respect to time. The rate of decrease in friction coefficient values at the start of the tests for each oil correspond to the levels of volatile content as shown in Figure 7; with higher volatile content oils displaying greater reductions in friction coefficient than lower volatile content oils. This would be due to the evaporation of the volatiles during the test. Samples with less volatile content took longer for the oil to reach a constant friction coefficient value than those with higher volatile content. 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.

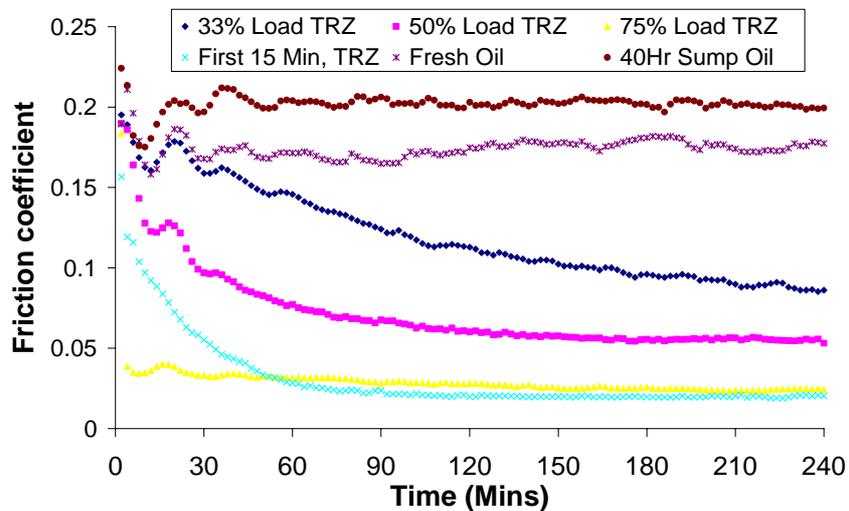


Figure 13: TE-77 friction coefficients with respect to time

The contact geometries of a 5mm diameter pin on a plate at reasonably low pressure of 2.6MPa under pure sliding will have resulted in predominantly hydroelastic lubrication with occasional mixed lubrication on film collapse at the end of the strokes. For this reason the friction coefficient values will predominantly be caused by the shearing of the lubricant and, therefore, the higher viscosity samples will tend to have higher friction coefficient values.

CONCLUSION

- A reliable method of sampling from the TRZ of an operating engine has been developed and used to extract relatively large (25ml) quantities of oil from the rear of the top piston ring of an operating engine for the first time.
- A range of oil samples have been subjected to a comprehensive range of chemical, rheological and tribological analysis. Distinct differences have been observed between the top ring zone samples and the fresh and sump oil samples. Correlations between the top ring zone oils with respect to the engine load at which they were sampled have also been observed.
- The results have clearly shown that the lubricant operating in the ring pack is tribologically different to that of the sump.

ACKNOWLEDGMENT

I would like to thank Martin Priest and Richard Chittenden at the University of Leeds for their discussions regarding this work as well as Moray Stark at the University of York Chemistry Department for help with the Chemical analysis. I also wish to thank Shell Global Solutions for funding the work.

REFERENCES

1. Kennedy, S. *Challenges for the additives industry in the 21st Century*. in *Additives 2005, Optimising Automotive Power Trains*. 2005. Dublin: RSC.
2. BP, *BP Statistical Review of World Energy in June 2001*. 2001, Beyond Petroleum, UK.
3. Yatsutomi, S., Y. Maeda, and T. Maeda, *Kinetic Approach to Engine Oil: 1 - Analysis of Lubricant Transport and Degradation in Engine System*. *Ind. Eng. Chem. Prod. Res. Dev.*, 1981. 20: p. 530.
4. Frottier, V. and J.B. Heywood, *Measurement of Gasoline Absorption into Engine Lubricating Oil*. SAE 961229, 1996.
5. Burnett, P.J., B. Bull, and R.J. Wetton, *Characterisation of the Ring Pack Lubrication and its Environment*. *I Mech E Part J: Journal of Engineering tribology*, 1995. 209(2): p. 109-118.
6. Saville, S.B., et al., *A Study of Lubricant Condition in the Piston Ring Zone of Single-Cylinder Diesel Engines Under Typical Operating Conditions*. SAE 881586, 1988.
7. Emanuel, N.M., E.T. Denisov, and K. Maizus Z, *Liquid Phase Oxidation of Hydrocarbons*. 1997, New York: Plenum Press.
8. Coates, J.P. and L. Setti, *Infrared Spectroscopy as a Tool for Monitoring Oil Degradation*. ASTM, 1984. STP 916: p. 57-78.
9. Coates, J.P. and L. Setti, *Analytical and Statistical Evaluation of Infrared Spectroscopy from used Diesel Lubricants*. SAE 841373, 1984.
10. Coates, J.P. and L. Setti, *Condition Monitoring of Crankcase Oils Using Computer Aided Infrared Spectroscopy*. SAE 831681, 1983.
11. Coates, J.P. and L. Setti, *Infrared Spectroscopy methods for Study of Lubricant Oxidation Products*. *ASLE Trans.*, 1985. 29(3): p. 394-401.
12. Williams, D.H. and I. Fleming, *Spectroscopic Methods in Organic Chemistry*, Revised. 1989, London: McGraw Hill Book Company.

APPENDIX

All experimental engine work undertaken during this project has been carried out using a single cylinder Hydra gasoline research engine (Ricardo Consulting Engineers Ltd.). This engine is quarter of a 1998cc 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 and the piston has a stroke and bore of 86mm, a compression ratio of 10.5:1 and a displacement of 499.5cc. In this configuration the engine has a maximum torque output of 36Nm. The engine is directly coupled to a swinging arm DC electrical dynamometer that can either motor the engine or absorb the power from the engine when fired.