This is a repository copy of *The effect of soot and diesel contamination on wear and friction of engine oil pump*.

White Rose Research Online URL for this paper:
http://eprints.whiterose.ac.uk/117141/

Version: Accepted Version

Article:

eprints@whiterose.ac.uk
https://eprints.whiterose.ac.uk/

Accepted Manuscript

The effect of soot and diesel contamination on wear and friction of engine oil pump

F. Motamen Salehi, A. Morina, A. Neville

Please cite this article as: Motamen Salehi F, Morina A, Neville A, The effect of soot and diesel contamination on wear and friction of engine oil pump, *Tribology International* (2017), doi: 10.1016/j.triboint.2017.05.041.

The Effect of Soot and Diesel contamination on Wear and Friction of Engine Oil Pump

F. Motamen Salehi*, A. Morina, A. Neville

Institute of Functional Surfaces (IFS), University of Leeds, Leeds, LS2 9JT, UK
Corresponding author: F.motamensalehi@leeds.ac.uk
Additional corresponding author: A.Neville@leeds.ac.uk

Abstract

The effect of oil contamination and oil degradation on friction and wear of engine oil pump are addressed in this paper. It provides a summary of an experimental study on the effects of oil contamination and oil degradation on tribological performance of a Variable Displacement Vane Pump (VDVP); a particular focus is on the vane-rotor contact. Firstly, a lab-based artificial ageing of fully-formulated engine oil (FFO) with the addition of contaminants such as carbon black (CB) and diesel is conducted. Secondly, the impact of these contaminants on the bulk property of the oil during the ageing process is investigated, using rheometry and Attenuated Total Reflectance/ Fourier Transform Infrared Spectroscopy (ATR/FTIR). Thirdly, the performance of these oils on friction and wear of the vane-rotor contact under boundary lubrication regime is evaluated. The wear mechanism and chemical nature of tribofilms formed in tribological tests are addressed using Scanning Electron Microscopy/Energy Dispersive X-ray analysis (SEM/EDX) and Raman spectroscopy. It is found that the consumption of the additives by soot (additive adsorption) in the engine oil during the ageing process has a significant effect on wear of the components. This mechanism has a higher impact on producing high wear than abrasion by soot particles.

Keywords: wear, abrasive, degradation, lubrication

1 Introduction

In recent years, there has been an increasing demand in the automotive industry to improve fuel economy. Poor fuel economy is closely linked to high friction of tribological components and can also lead to high wear. Designing fuel efficient vehicles is arguably the primary focus for all automotive industry [1, 2].

A Variable Displacement Vane Pump (hereafter denoted VDVP) is an innovative type of oil pump that has been introduced to the automotive industry to improve the efficiency of engines.

The VDVP is mainly composed of a slide ring with a circular inner bore, a rotor with several radially disposed vanes, a shaft, a spring and a casing. Figure 1 shows a schematic representative of the VDVP. The VDVP has a variable capacity that is adjustable to the engine demand, i.e. it only generates the flow rate required at any one time [3, 4]. Despite high efficiency and reduced power consumption, the VDVP has its own disadvantages in terms of high wear and friction in the components of the pump which can lead to failure of the pump.
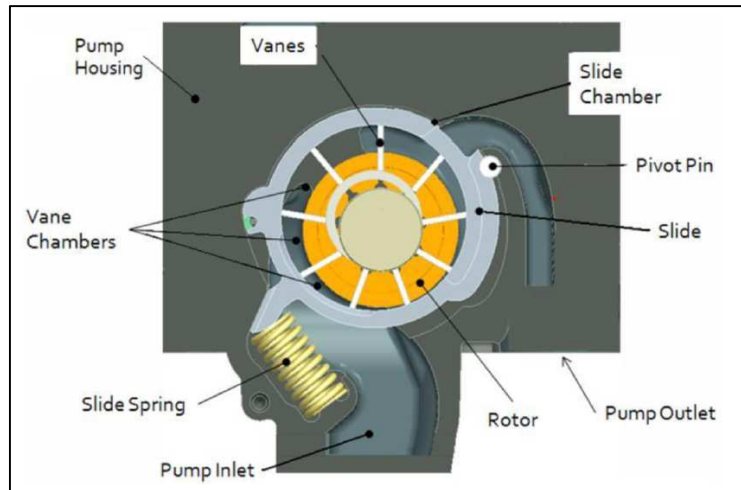
Figure 1. Schematic of Variable Displacement Vane Pump (VDVP) [5].

It has been reported that the wear occurring in vane-slide ring and vane-rotor contact is a critical aspect of the VDVP [4, 6]. Figure 2 shows the contact between the vane and rotor, which is designed to be a flat-on-flat reciprocating sliding contact, however when the vane tilts during the operation of VDVP, this contact will change to a line contact which causes severe wear on the vane faces. In this paper, the tribological behaviour of the vane-rotor contact is considered.

2
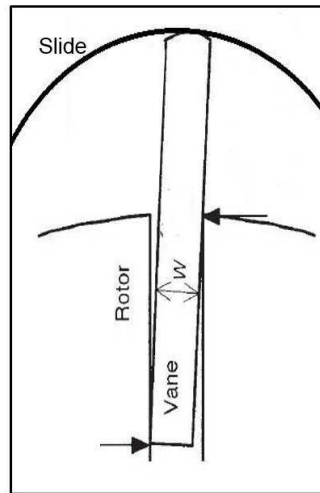
Figure 2. The contact between the vane and rotor in VDVP [5].

Many studies have been conducted to improve the efficiency of VDVP with the specific focus on factors such as design parameters and operating conditions [7-9]. One source of failure in VDVP is improper lubrication, a factor that has not been studied in detail. The contacts in the VDVP are sensitive to contamination due to the small clearances between the components [10]. Therefore it is essential to understand how oil contamination affects the performance of the VDVP. Table 1 indicates the possible range of oil contaminants in diesel engines which can potentially influence the tribological performance of the system [3, 4].

Table 1. Oil contamination types and their problems [1].

Type	Source	Major problems
Soot	Combustion blow-by	Interfere with additives, abrasive wear, heavy deposits, and oil thickening
Fuel	Blow-by-rich mixture	Oil breakdown
Oxidation of oil	Thermal degradation/ contact with atmospheric air	Oil thickening
Water	Combustion blow by-coolant leakage	Metal corrosion, promotes oil breakdown
Acids	Combustion blow-by, oil breakdown	Metal corrosion, autocatalysis of oil breakdown
Exhaust gases	Combustion blow-by	Acids promoting oil breakdown
Glycol	Coolant leakage	Oil breakdown
Metal Oxides	Component wear, oxidation of metallic particles	Abrasion, surface roughening leading to adhesion
Metallic particles	Component wear	Abrasion, surface roughening leading to adhesion, catalysis of oil breakdown
Minerals and dirt	Induction air	Abrasion, surface roughening leading to adhesion

Oil contamination such as that affected by soot and diesel influence the physical and chemical properties of the oil thus changing the tribological performance of VDVP. Soot is also known

3

to induce high wear in engine components. The effect of soot contamination in engine oils on wear of engine components have been investigated in many studies [11-19]. Various mechanisms have been proposed by which soot induces high wear.

Abrasion is the most accepted mechanism [13, 15-19]. It has been reported [20-23] that soot particles are hard enough to abrade both tribofilms formed on the surfaces and metallic engine components. Torrance [13] and Cadman et al. [16] postulated that soot removes the antiwear tribofilm formed on the surfaces and exposes a fresh reaction underlying metallic surface. Some other studies [23-25] suggested that soot in the oil can accumulate at the contact inlet and causes high wear due to the starvation of oil in the contact. It has also been reported [26] that soot competes with antiwear additives in adsorbing on the surface. The adsorption of soot on the surface prevents the adsorption of antiwear additives and their subsequent decomposition to form antiwear films. Additive adsorption on soot particles is another possible mechanism. It has been reported [11, 23, 27] that soot adsorbs antiwear additives in the oil phase reducing the concentration of the additives in the oil. Consequently, less antiwear additives adsorb at the contact interface to form antiwear films. A corrosive-abrasive mechanism has been recently reported by several studies [19, 27]. Olomolehin et al. [19] demonstrated that the interaction of CB and ZDDP in the oil can lead to aggressive wear. Although, there has been many studies on soot contamination, the actual mechanisms of wear caused by soot and its interaction with additives are not clearly understood.

Diesel fuel contamination can also cause starvation and deposits which reduce the functionality of the oil [28]. The effect of fuel contamination on the performance of oil is normally underestimated compared to the other contaminants such as soot and water. Fuel normally enters the engine oil through internal leakage of the injector and contaminates the oil [28].

Oil ageing is a destructive mechanism that can affect the physical and chemical properties of an oil and reduce its performance. Some factors such as temperature, metal content, type of base oil and additives, contamination content and the rate of air circulation influence the ageing rate of oil [29]. Kreuz et al. [30] showed that the high engine temperature significantly affected the ageing process of the oil. Zhang et al. [31] showed that the ageing process resulted in the formation of decomposition products and acids. It is thus necessary to understand the mechanisms of degradation and its impact on the oil properties and performance. This study aims to investigate the effect of oil contamination (soot and diesel) and oil degradation on wear and friction of the vane-rotor contact in VDVP.

2 Experimental procedures

2.1 Test lubricants

In order to have reliable and repeatable results, oil with consistent properties was needed for the experiments. Therefore, used engine oil extracted from an operational vehicle could not be used in the experiments since it would likely vary from car to car. An alternative approach was taken which was based on degrading the engine oil artificially in the lab in accordance to a novel ageing procedure [32, 33].

A commercially available synthetic fully-formulated engine oil with a viscosity grade of 5W-30 was selected. Table 2 shows the physical properties of this oil. 200 ml of oil was placed in a glass bottle covered with a three-neck lid as shown in Figure 3. The middle neck was equipped with a condenser to prevent the evaporation of the oil. Air was also passed to the beaker with the air flow of 10 L/h to provide a source of oxygen. Metal samples were also used to provide catalytic reactive surfaces. One of the necks was allocated to the sampling of the oil and condition monitoring of the system. The beaker containing oil was placed on a hot plate in a constant temperature at 160°C. Since the main degradation of lubricant occurs in the combustion chamber this temperature was selected to simulate the same conditions. This ageing method takes 96 hours and stresses the oil similar to 10,000 miles of severe vehicle service [34]. This method created a harsh condition in order to accelerate degradation of the oil. Figure 4 shows the oil colour changes with degradation time (0 hour to 96 hours of ageing). Since the fresh oil was clear and the oil got darker with ageing, the colour change can suggest that chemical modifications of the oil.
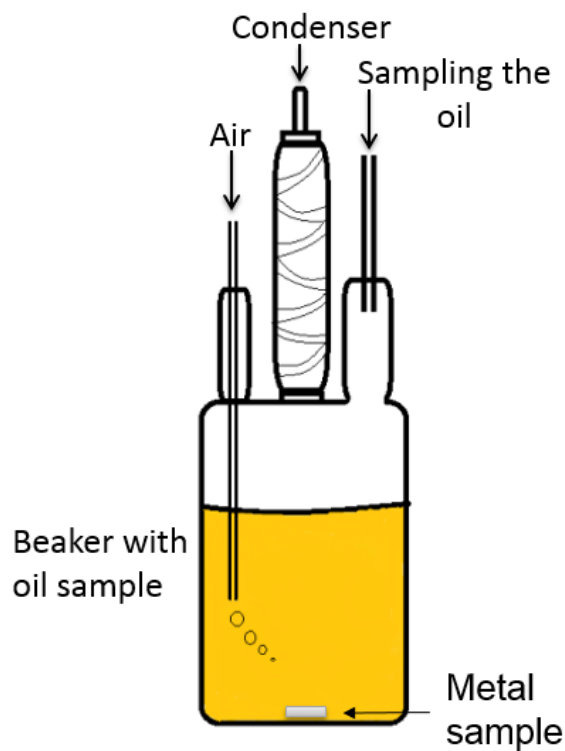
Figure 3. Schematic set-up for oil degradation.

Table 2. Physical and chemical properties of fresh engine oil.

Item	5W-30
Density at 15°C	0.860 g/ml
Flash point, CoC	250 °C
Kinematic viscosity at 40°C	57 mm^2/s
Kinematic viscosity at 100°C	10.0 mm^2/s
Total acid number	1.3 mgKOH/g
Ca concentration	1950 ppm
Zn concentration	640 ppm
P concentration	710 ppm
S concentration	1960 ppm

6

(a)   (b)   (c)   (d)   (e)

Figure 4. Visual inspection of (a) fresh FFO and oils after different ageing times:
(b) 24h, (c) 48h, (d) 72h, (e) 96h.

Carbon black is a good surrogate soot since it can be repeatedly and reliably sourced. A commercially-available carbon black (CB) (Monarch 120) was obtained from Cabot Corporation to simulate the engine soot. The size of soot particles from diesel combustion is approximately 40-45 nm diameter [14, 35]. Individual carbon black particles were measured by Scanning Transmission Electron Microscope (STEM) to be 50 nm diameter. The size of agglomerated particles are around 100 nm diameter. The hardness of Monarch 120 carbon black is reported close to the range metal engine components [36]. The diesel fuel used in this study was Shell City Diesel, sourced from a local petrol station (Shell Fuel Station, Leeds, UK).

Table 3 illustrates the test matrix for thermo-oxidative degradation tests. The effect of these contaminants on physical and chemical properties of FFO during the ageing process will be investigated.

Table 3. Contaminants and their level in the test matrix. CB was used as surrogate of soot.

Factors	Level (weight %)	Sample name	Ageing time
Oxidation	No contamination	Aged FFO (AFFO)	
Diesel	1 wt%	1% D	
CB	1 wt%	1% CB	96 hours (sampling every 24 h)
CB and diesel	1 wt% each	1% CB&D	
CB and diesel	2 wt% each	2% CB&D	

2.2 Tribometer test rig

All experiments were conducted using a TE77 tribometer test rig which operates under reciprocating sliding conditions. Tests in TE77 were conducted using SAE 52100 vane samples which are hardened and tempered to 57- 67 HRC hardness. Rotor was sintered metal (MP IF FD 0408-50) with 73- 93 HRB hardness. Figure 5 shows the schematic of the vane and rotor contact in the test set up. This test set up simulates the contact between vane and rotor in the real pump as shown in Figure 2.

The contact between rotor and vane which is a line contact was lubricated under a static volume of oil (10 ml). A load of 180 N was applied providing the initial contact pressure of 0.83 GPa at a frequency of 25 Hz. These test conditions simulate the contact in a vane pump. The test duration and test temperature were set for two hours and 100 °C respectively. The only variable in the experiments was the oil. For oil samples containing CB, a magnetic stirrer was used for 30 minutes to mix CB in oil. Then the oil samples were placed in an ultrasonic bath for another 30 minutes prior to both oil analysis and tribological tests. This has been done to ensure that the CB particles are homogenous in the oil and reduce the experimental deviation. All experiments were conducted three times to check for repeatability.

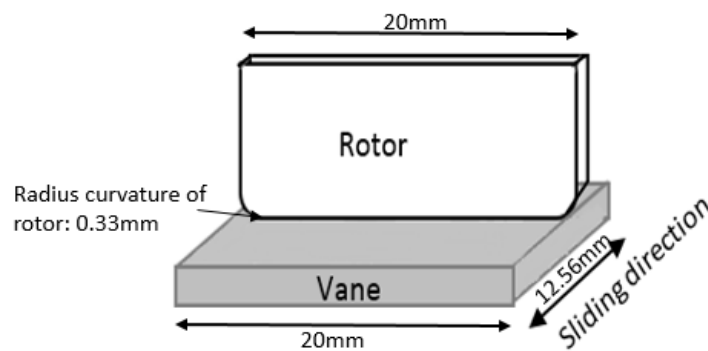**Figure 5 Schematic of tribotest set up for rotor and vane contact in TE77 tribometer.**

2.3 Post-test analysis

2.3.1 Viscosity measurement

A Kinexus rheometer from Malvern, UK was used to measure the viscosity of the oils in accordance to ASTM D445 standard. This rheometer was calibrated using the VHG® viscosity standard oil from LGC, UK which has the certified viscosity values at 40°C and 100°C respectively.

2.3.2 Attenuated Total Reflectance/ Fourier Transform InfraRed spectroscopy (ATR/ FTIR)

Attenuated Total Reflectance/ Fourier Transform InfraRed spectroscopy (ATR/ FTIR) was used to monitor the oil condition during the ageing process and to identify different chemical bonds of samples from measuring the absorption of various infrared light wavelengths. A Perkin Elmer FTIR spectrometer within the range of 650- 4000 cm^{-1} was used and the resolution of collected spectra was 4 cm^{-1}. First the background spectra was conducted then the oil samples were analysed. Data from the samples at 0 h and 96 h have been presented here.

2.3.3 Wear analysis

The influence of oil degradation and contamination on wear was examined by calculating the wear volume loss on vane samples. It is worth noting that higher wear was observed on the vane in comparison to the rotor. This is due to the greater hardness of the rotor material when compared with the vane materials as explained in section 2.2. Also, due to the complex shape of deformation and lower wear, the wear volume loss could not be accurately measured on the rotors. Therefore, the wear track on vane samples was only measured and further analysed in terms of chemical composition. Bruker's NPFLEX based on Wyko (WLI) technology was used to measure the volume loss on vane samples after tribotests to assess the wear. The specific wear coefficients were then calculated using the Archard wear equation, which is as follows:

$$K = \frac{V}{F \times S} \qquad Equation\ 1$$

Where F is the normal load (N), S is the sliding distance (m), V is the wear volume (m^3) and K is the dimensional wear coefficient (m^3/Nm).

2.3.4 Surface characterisation

Chemical characterisation of generated wear scars after testing was conducted using EDX analysis and Raman spectroscopy. A Carl Zeiss (Oberkochen, Germany) EVO MA15 Scanning Electron Microscope (SEM) was used in this study in order to take high magnification images of the sample surfaces. This microscope was also equipped with an Oxford Instruments (Abingdon, UK) XMAX Energy Dispersive X-Ray (EDX) spectrometer to elemental composition of tribofilm formed on the wear scars. SEM images and EDX spectra were recorded at both 20 Kev and 10 keV incident beam energy.

Raman analysis was also carried out using a Renishaw InVia spectrometer (UK). All spectra reported in this study were obtained with 488-nm wavelength laser. Peaks were analysed using the Renishaw WiRE program. All spectra were obtained at the room temperature. To check for uniformity in chemical composition, different positions of the sample were selected for the measurement in both EDX and Raman.

3 Results and discussion

3.1 Physical properties of lubricants

Figure 6(a) and Figure 6(b) show the dynamic viscosity of oils containing various contaminants at 40ºC and 100ºC respectively. It can be observed that the viscosity of the oils increased during the ageing process by the oxidation process and the addition of CB contamination. This increase was expected due to the oxidation of the oil [37]. Diesel contamination slightly reduced viscosity of the oil samples. The combination of diesel and CB contamination also reduced the viscosity of the oil samples. Viscosity values at 100ºC were quite constant and didn't show any significant differences. This can be related to the additives in FFO that protect the oil [38]. Viscosity modifiers have proven to be beneficial in controlling the soot-related viscosity changes [39]. Devlin et al. [21] showed that oils containing polymers and dispersants have excellent viscosity control in the presence of soot particles.

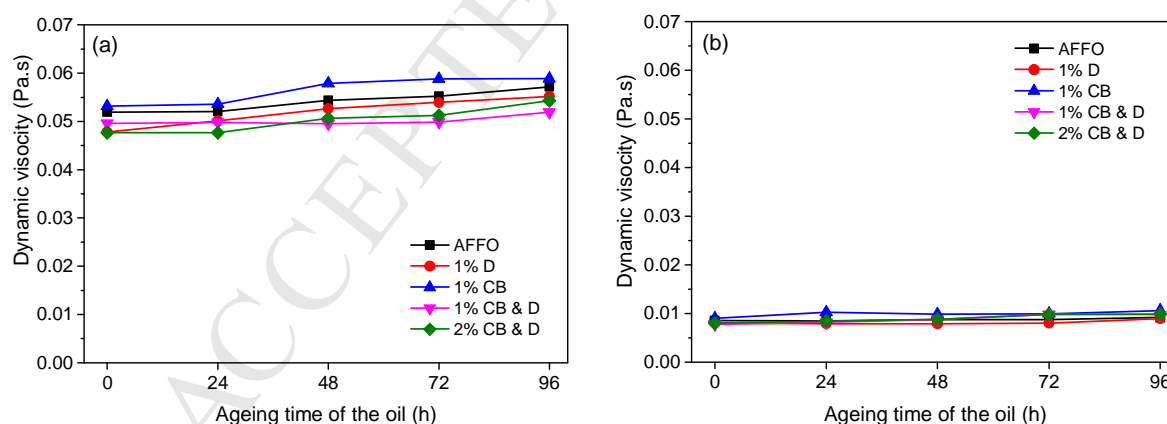**Figure 6 Dynamic viscosity of aged oil samples at different ageing times at (a) 40ºC and (b) 100ºC.**

3.2 Oil chemical composition

Figure 7 (a) shows FTIR spectrum of FFO at 0 h and 96 h. Infrared spectra of the aged oil due to oxidation showed similar absorption bands at 0 h and 96 h. IR bands between 2850-3000 cm^{-1} and 1385-1500 cm^{-1} are attributed to alkyl C-H stretching and C-H bending respectively.

The spectrum at 722 cm^{-1} is also attributed to alkyls chains [40]. These three main peaks which are from the base stock hydrocarbons were present in all oil samples.

Anti-wear (970 cm^{-1}), antioxidants (1080 cm^{-1}), viscosity improvers (1162 cm^{-1}), dispersants (1232 cm^{-1}) are known through literature (Figure 7 (b)) [41, 42]. Intensity of the bands at 1080 cm^{-1} and 1162 cm^{-1} increased and broadened. Such increase in intensity and band broadening after 96 h of the ageing can be attributed to the formation of several oxidation products due to the ageing process [43].

P-O-C bond from ZDDP additive in FFO is located at 920-1050 cm^{-1} region and the P=S bond is around 950-1040 cm^{-1} [44]. In the current study, the peak at 970 cm^{-1} is attributed to ZDDP. FTIR peaks showed a reduction in the intensity of infrared peak at 970 cm^{-1} after 96 h of ageing. In addition, an increase in the carbonyl absorbency at 1720 cm^{-1} (carboxylic acid) was observed which is attributed to the oxidative reaction of the lubricant. The formation of carboxylic acid during the ageing process is a good indicator of oil degradation.

11
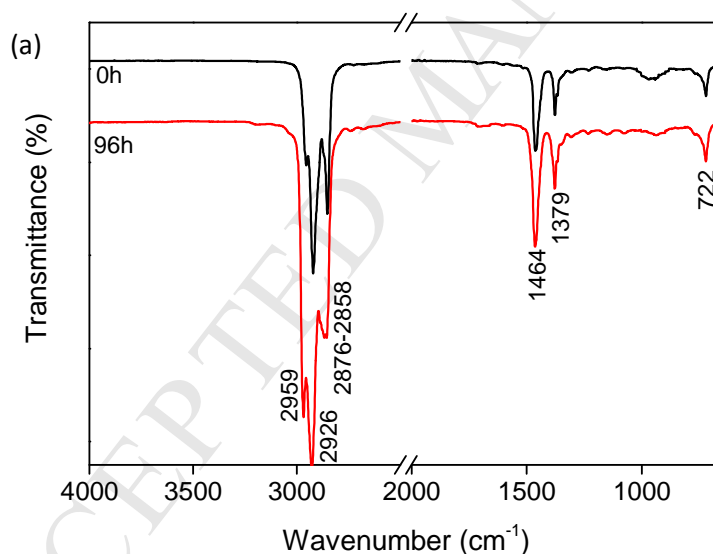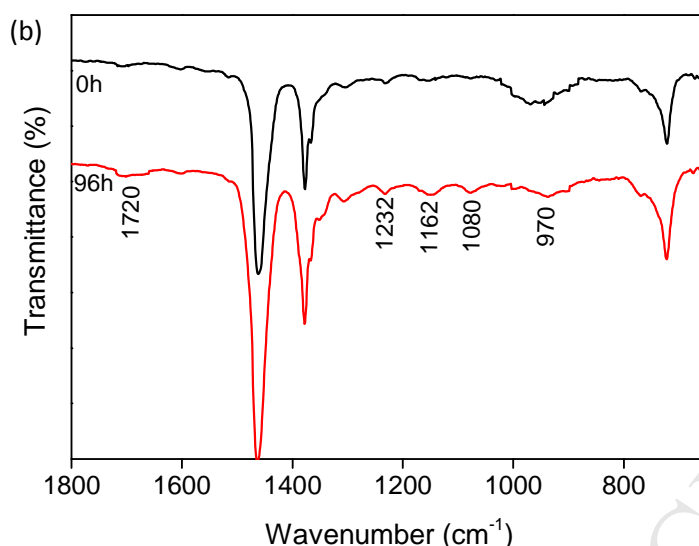
Figure 7 FTIR spectrum comparison of aged FFO at 0 h and 96 h (a) full spectra , (b) fingerprint region

For diesel contamination, as can be seen in Figure 8 a new peaks appeared during the ageing process. This peak is attributed to the sulphate peak (1040 cm^{-1}). Sulphate compounds can either be related to the sulphur in diesel fuel or the oxidation of sulphur from the additives in FFO [45]. Since this peak was not observed in the aged FFO, therefore the existence of this band can be due to sulphur in diesel. The presence of sulphur in diesel fuel has been confirmed by Raman analysis which showed a peak at 1609 cm^{-1}. It should be noted that the oxidation peak at 1720 cm^{-1} appeared in diesel-contaminated oil after 96 hours of ageing.
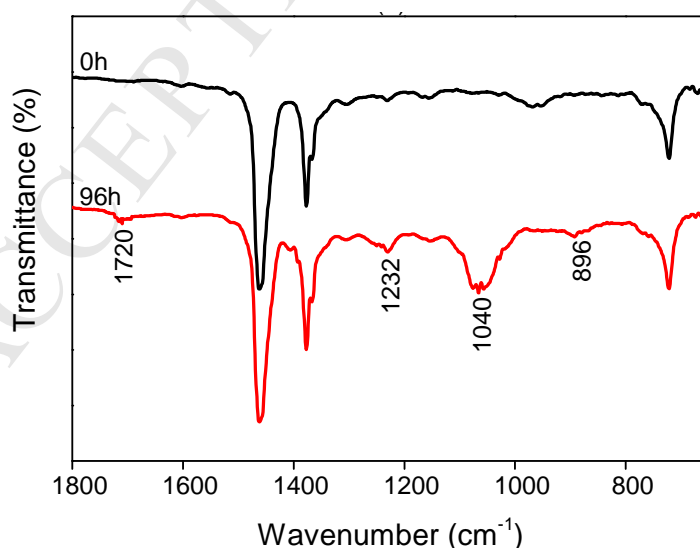
Figure 8 FTIR spectrum of fingerprint region for diesel contaminated oil at 0 h and 96 h.

Figure 9 indicates the FTIR band of FFO, contaminated oil with 1wt% and 2wt% CB and diesel. It can be seen that the intensity of antiwear additive peak (970 cm^{-1}) is reduced after 96 hours of ageing. This can be due to the additive adsorption on CB particles or additive depletion during the ageing process [19]. In general, the results suggest that under the condition of high temperature and exposure to air, oil has gone through partial oxidation to form a range of components such as weak acids and experienced some levels of degradation.
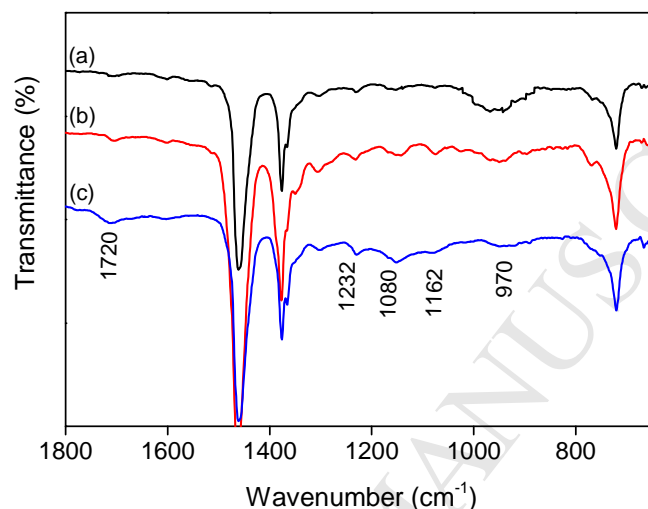
Figure 9 FTIR spectrum comparison of (a) FFO (b) aged oil with 1wt % CB&D and (c) aged oil with 2 wt% CB&D

3.3 Effect of oil degradation on friction and wear

The effect of the ageing of the oil on friction and wear of vane-rotor contact was studied. Figure 10 indicates the average friction coefficient values for the last 30 minutes of the tests (steady state friction). Figure 11 also shows the wear coefficient calculated using Equation 1 as a function of ageing time of the oil for various contaminated oils.

As can be seen in Figure 10 and Figure 11, in terms of aged FFO and diesel-contaminated oil, friction and wear were fairly unaffected during the ageing process. As can be seen from FTIR results in section 3.2, the intensity of additives reduced, however the additives are still present in the aged oils. Therefore, the low friction and wear results indicate that the additives can still protect the surfaces from friction and wear. This behaviour is thought to be due to the additives in FFO which delayed the oxidation process [38]. There have been several debates on the effect of ageing on the tribological performance of oils containing ZDDP. Devlin et al. [46] showed that tribofilm characteristics are different when using fresh oil and aged oils. Barnes et al. [47]

stated that the degradation of ZDDP could either increase or decrease wear based on different mechanisms. Coy et al. [48] reported that the aged oils containing ZDDP provided better wear performance than the fresh oils. A lot of previous research works [49, 50] have shown that the antiwear protection ability of ZDDP in the oil is due to its decomposition. They believed that the ageing of the oil results in decomposition of ZDDP which reduces the wear. On the other hand Devlin et al. [46] reported that the ability of ZDDP additives in aged oil to reduce friction and wear greatly depend on the engine operating conditions and ZDDP structure. In the present study, wear is still low even after ageing the oil which suggests that ZDDP is able to protect the surface even after 96 h of ageing. To confirm this, surface characterization is conducted to investigate the tribofilm of wear scar using both fresh and aged oils.

The greatest effect on friction and wear was observed when CB particles were present in FFO during the ageing process. When 1 wt% CB was added to the FFO, nearly 8% reduction in friction was observed. The same reduction in friction was observed when both CB and diesel were added to the oil. Also, higher levels of CB and diesel in oil decreased the friction further. These results are in line with Panchaliah et al [1] who stated that the combination of all contaminants produced lower friction values than the individual factors and uncontaminated oil. This decrease in friction can be attributed to the existence of CB in oil. It has been shown that CB can provide low friction and act as a solid lubricant, specifically in FFO which contains good dispersants [51]. It is thus believed that CB can act as a friction modifier since it has a similar structure to that of graphite, a well-known solid lubricant. Also, from the wear results in Figure 11, it is evident that reduction in friction comes at the price of high wear.

From the wear results, it can be seen that the wear was significantly higher when CB exists in the oil, almost three times more than the uncontaminated oil. This is consistent with the other literature [14, 51]. The combination of CB and diesel contamination increased the wear further. Wear also increased significantly during the ageing process from 0 to 96 hours. This can be attributed to lack of tribofilm formation due to the additive depletion or additive adsorption on CB particles during the ageing process.
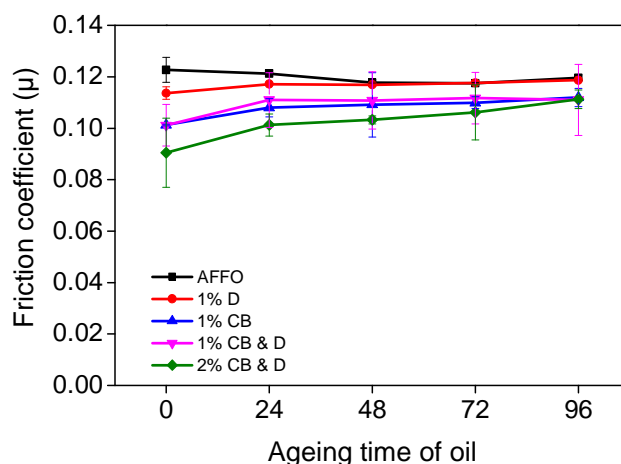
Figure 10 Steady state friction coefficient as a function of ageing time of the oil with aged oil due to oxidation, 1wt% diesel, 1wt% CB, 1wt% CB and diesel, and 2wt% CB and diesel. The error bars on the each points show the repeatability of tests. All tests were conducted at 100ºC.
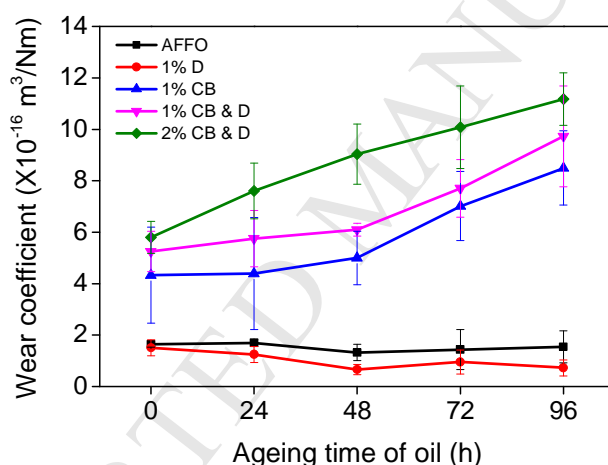
Figure 11 Wear coefficient as a function of ageing time of the oil with aged oil containing various contaminants. Wear measurements were conducted on the vane samples. All tests were conducted at 100ºC.

In general, tribological tests show that the influence of different contaminants and ageing time of the oil on friction and wear is complex. In order to find out the exact wear mechanism and elemental composition of tribofilm, further investigations were conducted which are presented in the following sections.

3.4 Surface characterisation

Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX) and Raman analysis on the worn surfaces were undertaken. Figure 12 shows the SEM images of

15

wear scars formed using FFO and diesel contaminated oil at 0 h and 96 h. The wear scar in Figure 12(a) showed slightly or nearly no marks on the surface. The arrow on the image indicates the sliding direction. There are other scratches on the sample which are possibly from the manufacturing since they are not in line with the sliding direction. EDX information on the wear track formed by FFO revealed the existence of Zn, P, and S elements with concentration of 0.41%, 0.19% and 0.15% by atomic% respectively. It should be noted that these values change from point to point of wear scar. This clearly illustrates the heterogeneous nature of tribofilm. Figure 12(b) shows SEM image of wear scar formed by diesel-contaminated oil. In the presence of diesel, EDX showed a higher concentration of S element (0.2 at%) in tribofilm.

Figure 13(a) indicates the Raman spectra obtained from the wear scar formed after test with FFO at both 0 h and 96 h. The Raman spectra also showed the presence of iron sulphide (FeS) evidenced by the broad peak at 200-400 cm^{-1}. The peaks observed at 670 cm^{-1} and 800 cm^{-1} were assigned to Iron (III) oxide (Fe_3O_4) and calcium hydroxide respectively. Phosphate peak can be seen at 987 cm^{-1} and zinc phosphate peak observed at 1040 cm^{-1} [52]. The presence of phosphate films in the wear scars was due to decomposition of ZDDP additive which was present in the FFO. The presence of phosphate and zinc phosphate tribofilm within wear scars with FFO are consistent with the low wear observed by FFO in Figure 11. The same peaks were observed within the wear scar of aged FFO after 96 h of ageing with lower intensity. Figure 13 (b) shows Raman spectra obtained from wear scar after tests with diesel contaminated oil at 0 h and 96 h. The results showed the presence of iron oxide, calcium hydroxide, iron oxide and phosphate peak. These spectra showed similar peaks presented in tribofilm formed on the wear scar by FFO.
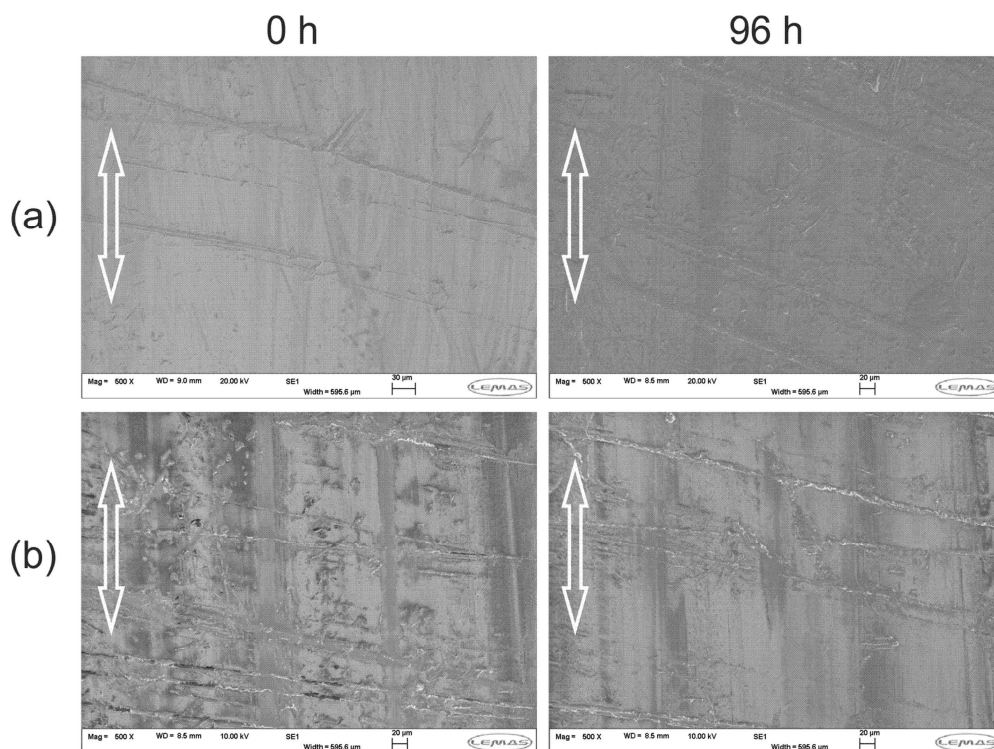
Figure 12 SEM images of wear scar formed by (a) FFO (b) 1wt% diesel-contaminated oil at 0 h and 96 h of oil ageing.
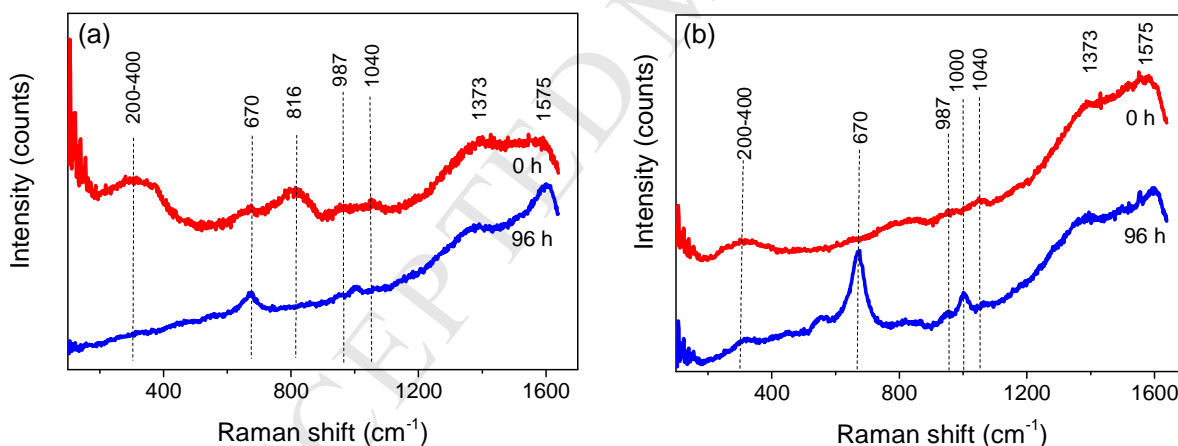
Figure 13 Raman spectra of wear scars after tests with (a) FFO and (b) 1wt% diesel-contaminated oil.

Figure 14(a) and Figure 14(b) show the wear scar on the vane sample formed using aged oil with %1wt CB at 0h and 96 h respectively. It can be seen that abrasion increases during the ageing process from 0 h to 96 h. The same increase in abrasion was also observed for a combination of contaminants. The wear was much more severe when the oil was contaminated and aged with both CB and diesel (see Figure 14(c) and Figure 14(d)).

Moreover, EDX results revealed no elements of Zn, P and S after 96 h of ageing the oil for these samples. Figure 15(a) and Figure 15(b) show Raman spectra obtained from wear scar after tests with 1wt% CB and 1wt% CB and diesel at 0 h and 96 h of ageing time respectively. It can be seen that the generated wear scars were mainly composed of iron oxides after 96 h; haematite (Fe_2O_3) and magnetite (Fe_3O_4). The peaks at 222 cm^{-1}, 291 cm^{-1} and 404 cm^{-1} were assigned to Fe_2O_3 and the peak at 670 cm^{-1} was assigned to Fe_3O_4. The carbon peaks were also observed on the contact region at 1375-1575 cm^{-1}. These results are in line with the high wear observed when CB was present in oil after 96 h of ageing in section 3.3. The same results were observed for 2wt% CB and diesel contaminated oil. It has been suggested that soot adsorbs antiwear additives in the oil reducing the concentration of the additives in the lubricant. Consequently, less antiwear additives adsorb at the contact interface to form antiwear films [11].

ICP-OES was conducted on aged oil with 1wt% CB to determine the elemental content of additives in the oil after ageing process. As can be seen from Table 4, the concentration of additives reduced in oil due to additive depletion during the ageing process. Also, in order to determine anti- wear additive adsorption on CB particles, aged oil with 1% CB was centrifuged and filtered to separate CB particles then ICP-OES analysis was conducted. The ICP results showed that there was no elements of anti-wear additives remained in the oil after 96 h of ageing. EDX analysis was also conducted on the CB particles and results revealed the presence of phosphorous and zinc which are elements of ZDDP. These results suggest that additive adsorption on CB particles occurred during the ageing process. The same results observed in the aged oils with both diesel and CB.

Table 4. Elemental composition of the fresh oil and aged oil with 1wt% CB

	Concentration (ppm)		
Sample	Zn	P	S
Fresh FFO	640	710	1960
Aged oil with 1wt% CB	295	310	950
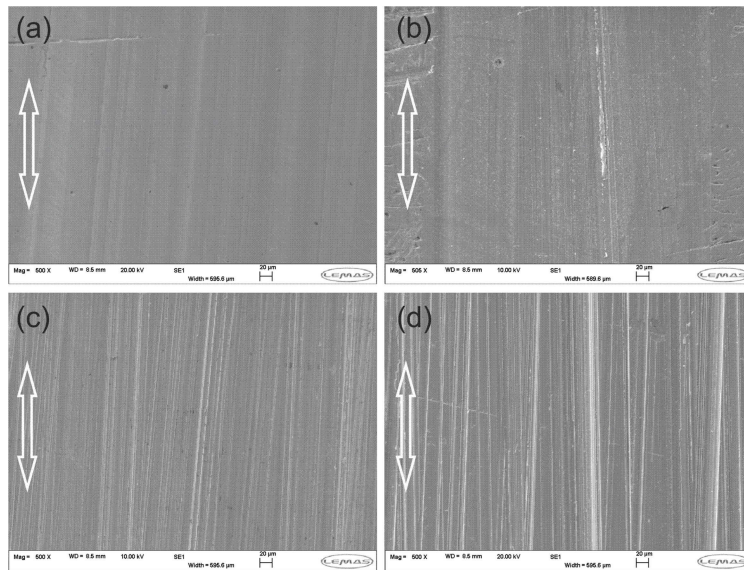
Figure 14 SEM images of wear scar on vane samples using (a) FFO with 1wt% CB at 0 h, (b) aged oil with 1wt% CB after 96 h, (c) aged oil with 1wt% CB&D after 96 h (d) aged oil with 2wt% CB&D a 96 h.
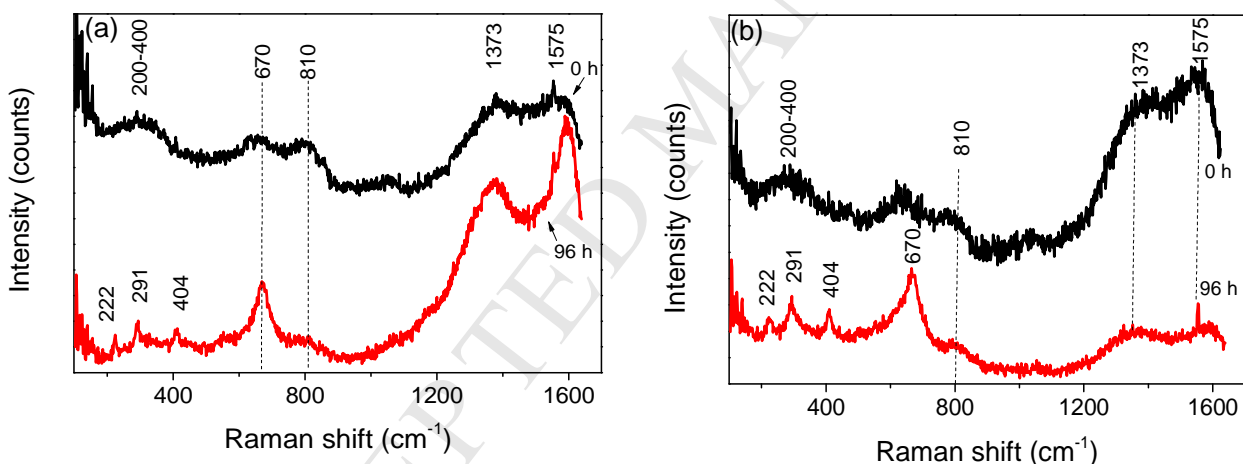
Figure 15 Raman spectra of wear scars after tests with (a) 1wt% CB and (b) 1wt% CB and diesel contaminated oil.

3.5 The effect of contaminants on wear mechanism

Based on the results obtained in the previous sections, further tests were carried out in order to investigate the antagonistic effect of diesel and soot contamination on wear. Table 5 shows the test matrix and aim of these experiments. Figure 16 indicates the average friction coefficient values for the last 30 minutes of the tests and wear coefficients calculated using Equation 1.

Table 5 Text matrix for ageing the oil.

Test	Test condition	Aim/Purpose

T1	☐	Aged oil with no contaminant for 96 h then add 1 wt% CB before the test	To establish the relationship between abrasion and ageing of the oil
T2	△	Aged oil with no contaminant for 96 h then add 2 wt% CB before the test	
T3	⬠	Aged oil with 1wt% diesel for 96 h then add 1 wt% CB before the test	To investigate the antagonistic effect of contaminants on wear
T4	☆	Aged oil with 1wt% CB for 96 h then add 1 wt% diesel before the test	
T5	○	Filter the aged oil with 2 wt% CB and diesel contaminants	To understand how oil functions after removing the CB contaminants
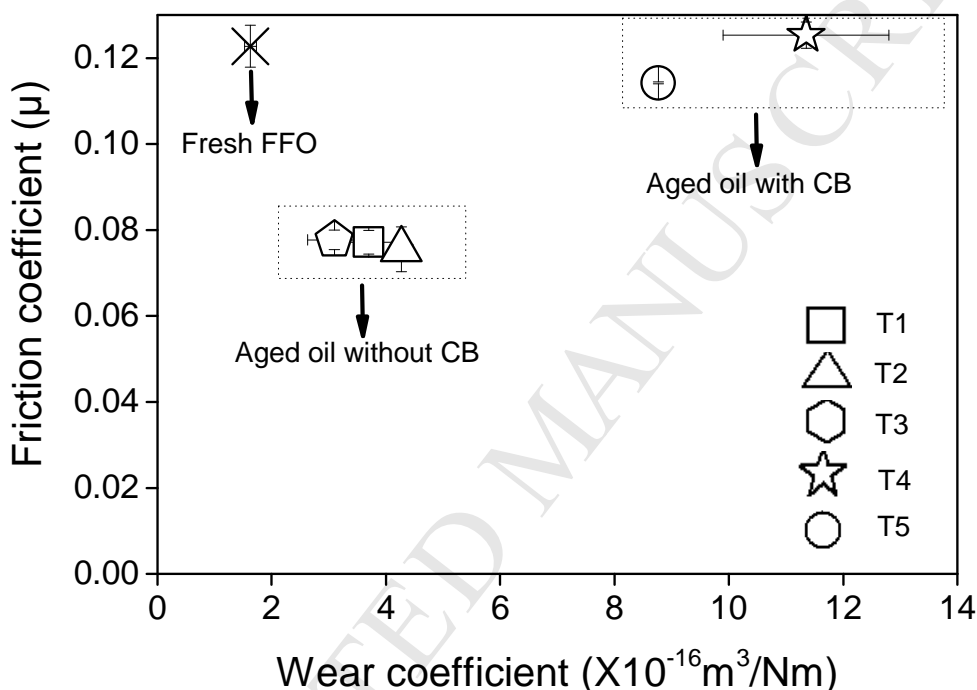
Figure 16 Friction and wear coefficient of tests. Wear measurements were conducted on vane samples. Error bars show repeatability of tests.

3.5.1 Effect of abrasion by CB

Tests T1 and T2 were conducted using aged FFO for 96 h then adding 1wt% and 2wt% CB in the oil respectively. These tests were conducted to establish why abrasion increases during the ageing procedure. Figure 16 indicates that friction reduced for both tests compared to the FFO. In the presence of CB particles wear increased and more CB particles in oil resulted in higher wear as expected.

Figure 17(a) shows the wear scar formed using aged oil with 1wt% CB for 96 h. Figure 17(b) and Figure 17(c) indicate the SEM images of wear scar for test T1 and T2 respectively. There

are a number of scratches in the direction of sliding on the wear scar produced during tests T1 and T2 however the wear is not as severe as wear scar shown in Figure 17(a). These results indicate that when 1wt% CB was present in the oil during the ageing process, approximately 42% higher wear was observed in comparison to the test in which 1wt% CB was added to the aged FFO (Figure 17(b)). That is to say although in both tests 1wt% CB was present in oil, the wear behaviour was different.

wear coefficient: 6.4   wear coefficient: 3.7   wear coefficient: 4.2
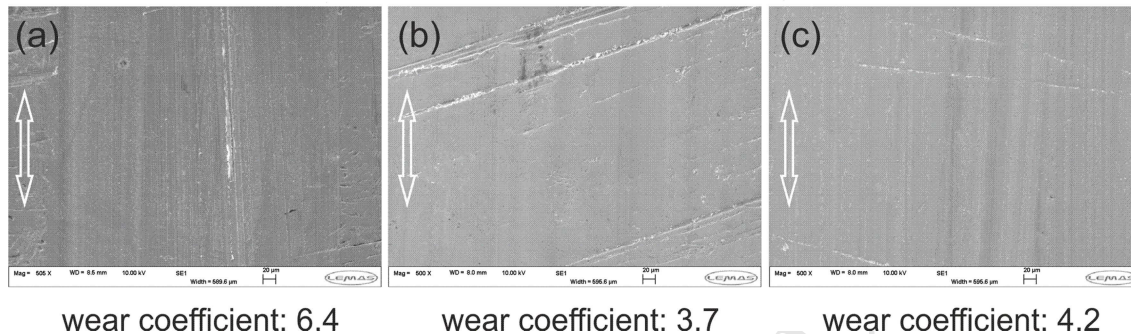
Figure 17 SEM images of wear scar on vane with (a) aged oil with 1wt% CB for 96 and aged FFO for 96h then adding (b) 1 wt% CB (c) 2wt% CB - Wear coefficient unit is ($\times 10^{-16}$ m^3/Nm).

Many studies [13, 15, 17, 18, 53] have reported that the increase in wear by soot was related to the abrasive nature of soot. The results presented in this study demonstrated that the tests which were conducted with the same levels of CB particles (1wt%) showed different levels of wear. Figure 18 compares the wear coefficient and the average depth of wear scars on sample using different oils. It can be seen that when the oil is aged in the presence of 1wt% CB for 96 h, average wear depth and wear coefficient are much higher than the oil which is aged with no CB then 1wt% CB was added before the test. The difference between the wear results with oils containing 1%wt CB suggests that abrasion is not the dominant wear mechanism, since similar wear would be expected with the same concentration of CB. Even higher levels of CB (2wt%) showed less amount of wear in comparison to the aged oil which contained 1wt% CB during the ageing process. Thus, it can be concluded that the high wear observed in aged oil containing 1wt% CB cannot be simply justified by abrasion. These results suggest that the presence of CB in the oil will not necessarily cause severe wear during the tribological tests due to abrasion or mechanical action. Thus, the results presented in this study contradict the concept that suggests abrasion-induced wear is the main mechanism [13, 15, 17, 18, 53].
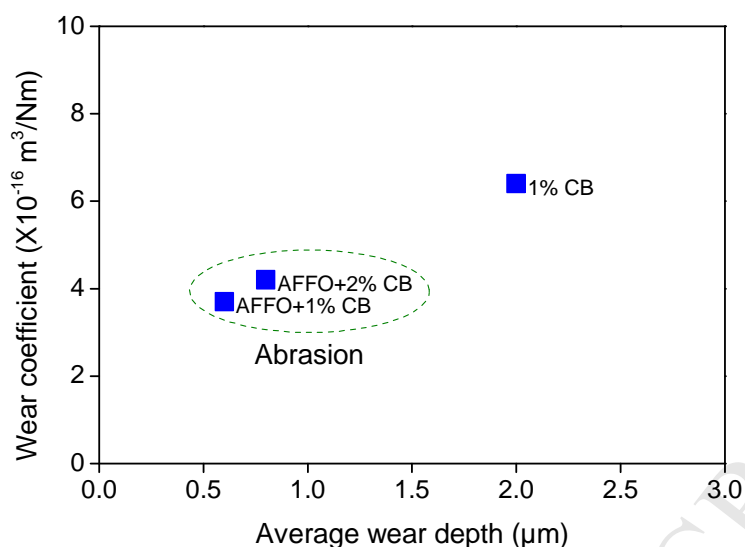
Figure 18 Wear coefficient and average wear depth of wear scar of vane samples using aged FFO with 1wt% CB, aged FFO then adding 1wt% and 2wt% CB.

3.5.2 Antiwear additive adsorption

The aged oil with 2 wt% CB and diesel was filtered to investigate how the oil would function after removing of the CB particles. The centrifuge was conducted for one hour with the speed of 12000 rpm to remove as many CB particles as possible. Tests with such oil provide wear results in which the effect of CB particles (third-body abrasion) was eliminated. As can be seen in Figure 19, the removal of CB from oil resulted in lower wear (21% reduction) compared to unfiltered oil. Figure 20 indicates the SEM images of wear scar formed by filtered and unfiltered oils. The wear coefficient was still high using filtered oil Therefore, the lack of tribofilm on the wear scars and metal-on-metal contact can be responsible for the high wear observed. This high wear can be explained by additive adsorption mechanism on soot particles [11, 23]. Raman analysis on the wear scar of T5 did not show any ZDDP elements in the tribofilm as shown in Figure 21. Therefore, the high wear and the lack of tribofilm on the wear scar suggest that even after removing of the CB particles the oil was not able to generate tribofilm. These results suggest that additive adsorption is the key wear mechanism.
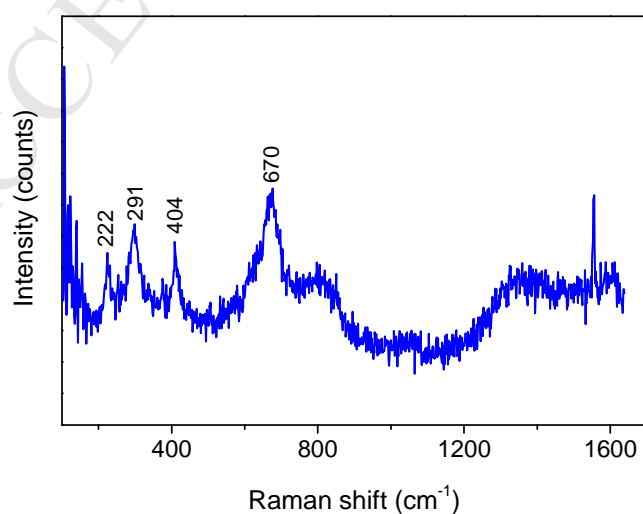
22
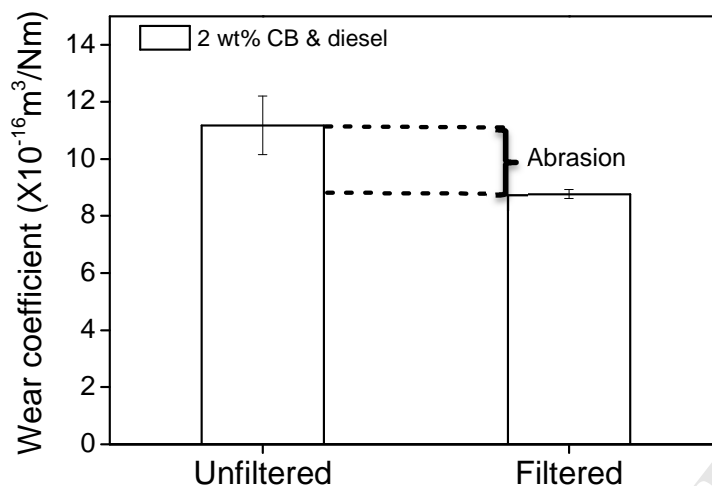
Figure 19 Wear coefficient for tests conducted with unfiltered and filtered FFO containing 2 wt% CB and diesel.
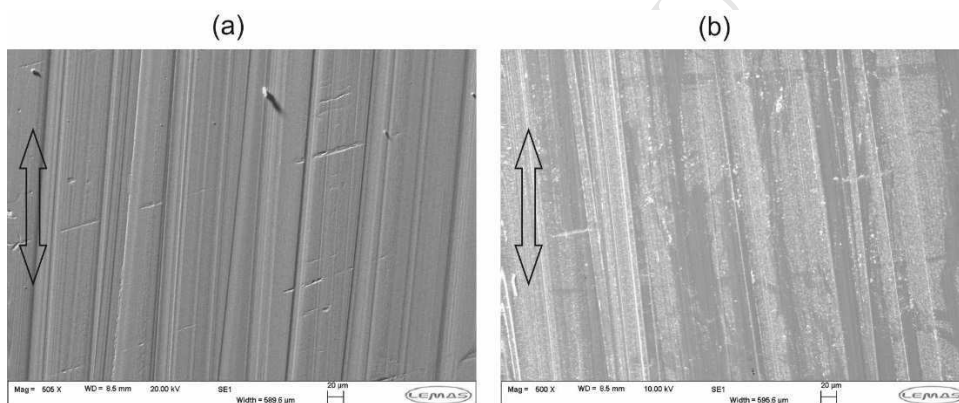
Figure 20 The wear scar formed on vane samples by aged oil with %2wt CB and diesel (a) non-filtered (b) filtered.


Figure 21 Raman spectra of wear scar of vane sample after tests with the filtered oil (T5).
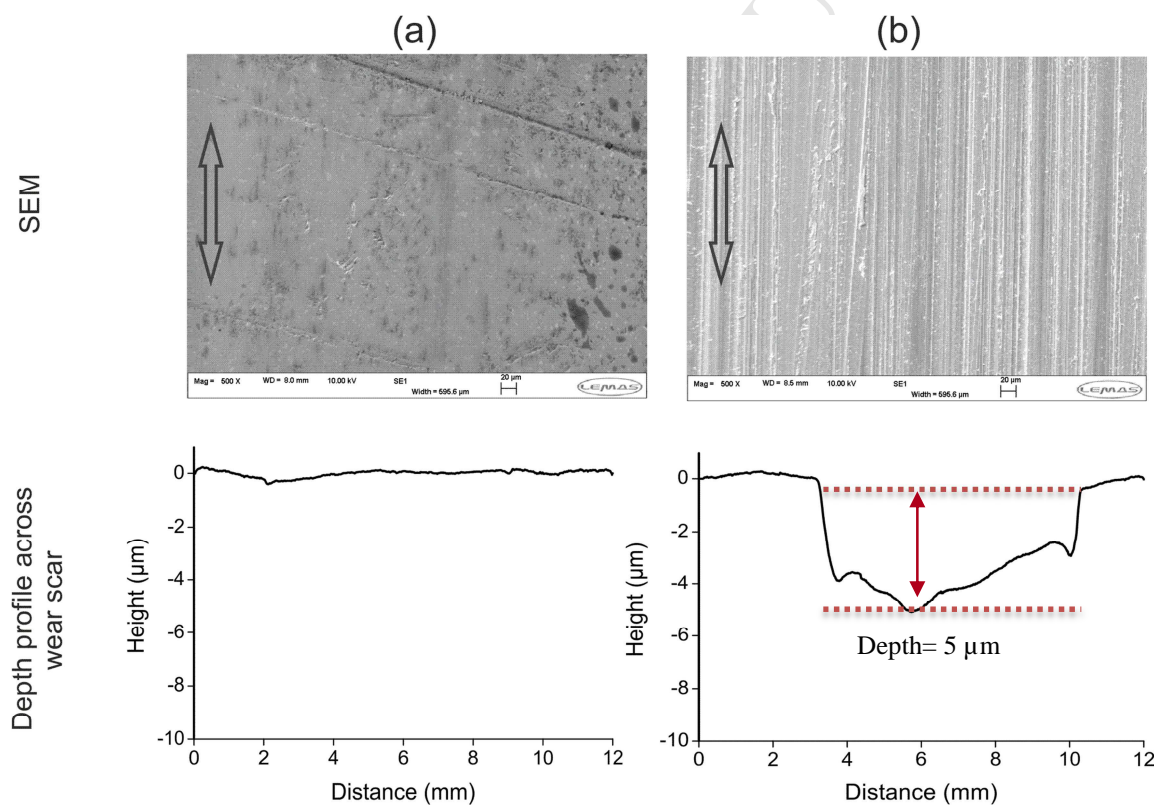
3.5.3 Antagonistic effect of contaminants on wear

The wear results in Figure 11 showed that the combination of CB and diesel had an antagonistic effect on wear compared to the individual effect of each contaminants on wear. Tests T3 and T4 were conducted to investigate this mechanism. The oil properties were not affected by diesel contamination during the ageing process as shown in Figure 6. Thus, when CB was added to the aged oil in test T3, the most likely wear mechanism was abrasion of tribofilm formed on the surfaces by CB particles as shown in Figure 22. When CB was present in FFO during the ageing process and then diesel was added before the tests, there are a combination of factors that produce high wear; such as the interaction between contaminants and additives during the ageing process (mainly additive adsorption) and abrasion by CB particles (Figure 22).

Figure 23(a) and Figure 23(b) show SEM images of the wear scar after tests with T3 and T4 which explained in Table 5. From the SEM images it can be seen that the wear was severe when the oil was aged with 1wt% CB for 96 h and the diesel was added just before the test. The reverse sequence resulted in less wear. Wear coefficient was approximately 73% higher in T4 than T3. In addition, the generated wear scar was about 5 µm deep in T4. It is believed [19] that abrasion by soot can either be due to the rubbing metallic surfaces or by rubbing the tribofilms formed on the surface. The latter mechanism was prominent in test T3. Tribofilms are softer than steel and therefore they are more vulnerable to abrasion by soot [54]. However, in test T4 both tribofilm and metallic surface were removed and resulted in a severe wear. Table 6 summarises the results and potential mechanism occurring in tests T3 and T4.
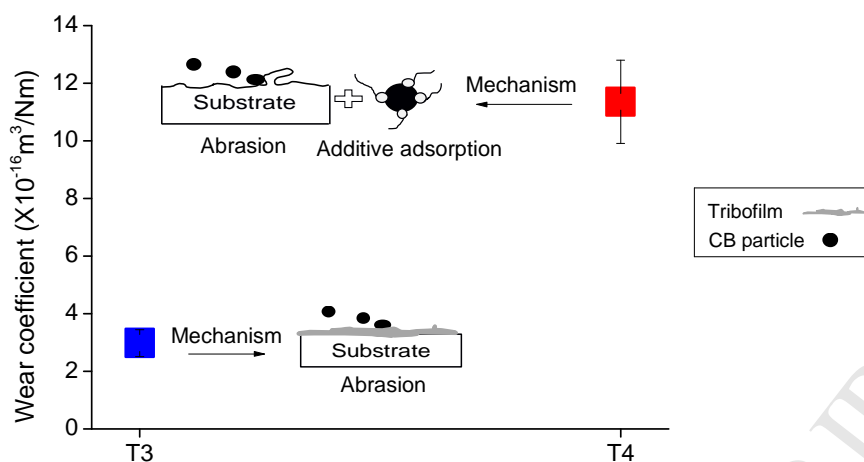
Figure 22 Comparison of wear results and potential wear mechanism between T3 (aged diesel-contaminated oil then adding 1wt% CB) and T4 (aged CB-contaminated oil then adding 1wt% diesel).

Figure 23 SEM images and wear scar depth for tests (a) T3 and (b) T4.

Table 6 Antagonistic effect of contaminants on wear.

Test	T3	T4
Causes of ageing	• Oxidation • Diesel	• Oxidation • CB particles
contaminants added after ageing (96h)	CB	Diesel
Effect of added contaminants	Abrasion	Oil dilution
Conclusions	• Not severe wear • Abrasion by CB was probably not the dominant mechanism of producing high wear • Tribofilm removal by CB particles	• Severe wear • Antiwear additives properties is lost during the ageing process as a result of additive adsorption • No tribofilm formed, therefore CB particles abrade steel surface

4   Conclusions

In this study friction and wear behaviour of vane components in VDVP were studied using various contaminants and varying ageing times. The results from FTIR, SEM/EDX and Raman analysis together provided a consistent explanation of the wear mechanism and surface chemistry. The results presented in this paper indicate that the ageing process on its own did not have a significant effect on the performance of FFO used in this study. However, when CB was present in FFO during the ageing process it led to more severe wear. This study contradicted all previous studies that suggested that abrasion (i.e. mechanical action) by CB particles is the main mechanism producing high wear in engine components [13, 15, 17, 18]. This study proves the role of more dominant wear mechanisms in the presence of CB particles (antiwear additives adsorption) which has a chemical nature.

Acknowledgment

References

1.   R. Penchaliah, T. J. Harvey, R. J. K. Wood, K. Nelson, and H. E. G. Powrie, *The effects of diesel contaminants on tribological performance on sliding steel on steel contacts.* Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology, 2011. **225**(8): p. 779-797.

2.   J. Merkisz, *Combustion engines development and real driving emissions* Journal of KONES Powertrain and Transport, 2014. **21**(2).

3.   D. OuYang, W. Cai, L. He, and Y. Li, *Two Types of Variable Displacement Oil Pump Development*, in *Proceedings of the FISITA 2012 World Automotive Congress: Volume 2: Advanced Internal Combustion Engines (II)*. 2013, Springer Berlin Heidelberg: Berlin, Heidelberg. p. 1357-1368.

4.   F. Frendo, N. Novi, and R. Squarcini. *Numerical and experimental analysis of variable displacement vane pumps*. in *AITC-AIT 2006- 5th International Conference on Tribology, *. 2006. Italy.

5.   P.E. Sullivan, *Internal Force Analysis of a Variable Displacement Vane Pump. Univ. of Toronto, Manmohan Sehmby Magna Powertrain, Inc.* SAE International, 2012.

6.   E. Mucchi, A. Agazzi, G. D'Elia, and G. Dalpiaz, *On the wear and lubrication regime in variable displacement vane pumps.* Wear, 2013. **306**(1–2): p. 36-46.

7.   M.R. Cho and D.C. Han, *Vane tip detachment in a positive displacement vane pump.* KSME International Journal, 1998. **12**(5): p. 881-887.

8.   D.B. Parker, *Positive displacement pumps-performance and application*, in *11th International Pump Users Symposium*. 1994.

9.   M. Rundo and N. Nervegna, *Geometry Assessment of Variable Displacement Vane Pumps.* Journal of Dynamic Systems, Measurement, and Control, 2006. **129**(4): p. 446-455.

10.   D.M. Pirro, M. Webster, and E. Daschner, *Lubrication Fundamentals, Revised and Expanded*. Third ed. 2016.

11.   F.G. Rounds, *Soots from used diesel-engine oils: their effects on wear as measured in 4-ball wear tests*. 1981, SAE International.

12.   D.A. Green and R. Lewis, *Investigation of Soot Contaminated Lubricant Wear Mechanisms*. 2007, SAE International.

13.   M. Torrance, *Wear of lubricated steel in the presence of dispersed carbon*, in *IMechE Mission of Tribology Conference*. 2004.

14.   D. A. Green and R. Lewis, *Effect of soot on oil properties and wear of engine components.* Journal of Physics D: Applied Physics, 2007. **40**(18): p. 5488.

15.   P.R. Ryason, I.Y. Chan, and J.T. Gilmore, *Polishing wear by soot.* Wear, 1990. **137**(1): p. 15-24.

16.   W. Cadman and J.H. Johnson, *The study of the effect of exhaust gas recirculation on engine wear in a heavy-duty diesel engine using analytical ferrography* SAE International, 1986.

17.   M. Ratoi, R. C. Castle, C. H. Bovington, and H. A. Spikes, *The influence of soot and dispersant on ZDDP film thickness and friction, Lubrication Science17.* 2004: p. 25-43.

18.   I. Nagai, H. Endo, H. Nakamura, and H. Yano, *Soot and Valve Train Wear in Passenger Car Diesel Engines, SAE Technical Paper 831757.* SAE International, 1983.

19.   Y. Olomolehin, R. Kapadia, and H. Spikes, *Antagonistic Interaction of Antiwear Additives and Carbon Black.* Tribology Letters, 2010. **37**(1): p. 49-58.

20.   T.C. Jao, S. Li, K. Yatsunami, S.J. Chen, A.A. Csontos, and J.M. Howe, *Soot characterisation and diesel engine wear.* Lubrication Science, 2004. **16**(2): p. 111-126.

21.   C. C. Devlin, C. A. Passut, R. L. Campbell, and T.C. Jao, *Biodiesel Fuel Effect on Diesel Engine Lubrication*. 2008, SAE International 2008-01-2375.

22.   M. Gautam, K. Chitoor, S. Balla, and M. Keane, *Contribution of Soot Contaminated Oils to Wear-Part II*. 1999, SAE International.

23.   D. A. Green and R. Lewis, *The effects of soot-contaminated engine oil on wear and friction: a review.* Automobile Engineering 2008. **222**(9): p. 1669-1689.

24.   T. Skurai and K. Yoshida, *Tribological Behaviour of Dispersed Phase Systems*, in *International Tribology*. 1987.

25.   D.A. Green, R. Lewis, and R.S. Dwyer-Joyce, *Wear effects and mechanisms of soot-contaminated automotive lubricants.* Engineering Tribology, 2006. **220**: p. 159-169.

26.   F.G. Rounds, *Carbon: Cause of Diesel Engine Wear? .* SAE International, 1977.

27. F. Motamen Salehi, D. N. Khaemba, A. Morina, and A. Neville, *Corrosive–Abrasive Wear Induced by Soot in Boundary Lubrication Regime.* Tribology Letters, 2016. **63**(2): p. 1-11.

28. S. Capone, M. Zuppa, D.S. Presicce, L. Francioso, F. Casino, and P. Siciliano, *Metal oxide gas sensor array for the detection of diesel fuel in engine oil.* Sensors and Actuators B: Chemical, 2008. **131**(1): p. 125-133.

29. W. Tuszynski, R. Michalczewski, W. Piekoszewski, and M. Szczerek, *Effect of ageing automotive gear oils on scuffing and pitting.* Tribology International, 2008. **41**(9–10): p. 875-888.

30. K.L. Kreuz, *Gasoline Engine Chemistry as Applied to Lubricant Problems.* Lubrication Science, 1969. **55**: p. 53-46.

31. X. Zhang, H. Murrenhoff, P. Weckes, and W. Hölderich, *Effect of temperature on the ageing behaviour of unsaturated ester-based lubricants.* Journal of Synthetic Lubrication, 2004. **21**(1): p. 1-11.

32. Ch. Besser, Ch. Schneidhofer, N. Dörr, F. Novotny-Farkas, and G. Allmaier, *Investigation of long-term engine oil performance using lab-based artificial ageing illustrated by the impact of ethanol as fuel component.* Tribology International, 2012. **46**(1): p. 174-182.

33. *CECL-48-A00: Oxidation stability of lubricating oils used in a utomotive transmissions by artificial ageing. Co-ordinating European Council for the Development of Performance Tests for Fuels, Lubricants and Other Fluids*. 2007.

34. S. Korcek, R.K. Jensen, and M.D. Johnson, *Assessment of the useful life of current long-drain and future low-phosphorus engine oils.* Tribotest, 2003. **9**(3): p. 197-207.

35. E. Hu, X. Hu, T. Liu, L. Fang, K.D. Dearn, and H. Xu, *The role of soot particles in the tribological behavior of engine lubricating oils.* Wear, 2013. **304**(1–2): p. 152-161.

36. M. T. Devlin, S. Li, T. Burgess, and T-C. Jao, *Film Formation Properties of Polymers in the Presence of Abrasive Contaminants*. 2002, SAE International 2002-01-2793.

37. A. Agoston, C. Ötsch, and B. Jakoby, *Viscosity sensors for engine oil condition monitoring—Application and interpretation of results.* Sensors and Actuators A: Physical, 2005. **121**(2): p. 327-332.

38. S. Aldajah, O.O. Ajayi, G.R. Fenske, and I.L. Goldblatt, *Effect of exhaust gas recirculation (EGR) contamination of diesel engine oil on wear.* Wear, 2007. **263**(1–6): p. 93-98.

39. S. George, S. Balla, V. Gautam, and M. Gautam, *Effect of diesel soot on lubricant oil viscosity.* Tribology International, 2007. **40**(5): p. 809-818.

40. D. Lin-Vien, N.B. Colthup, W.G. Fateley, and J.G. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*. 1991, New York: Academic Press.

41. M. Diaby, M. Sablier, A. Le Negrate, M. El Fassi, and J. Bocquet, *Understanding carbonaceous deposit formation resulting from engine oil degradation.* Carbon, 2009. **47**(2): p. 355-366.

42. J. Martínez and A.C. Aguiar, *Analytical Supercritical Fluid Extraction*, in *Analytical Separation Science*. 2015, Wiley-VCH Verlag GmbH & Co. KGaA.

43. Y. Arai and D.L. Sparks, *ATR–FTIR Spectroscopic Investigation on Phosphate Adsorption Mechanisms at the Ferrihydrite–Water Interface.* Journal of Colloid and Interface Science, 2001. **241**(2): p. 317-326.

44. A. Kupareva, P. Mäki-Arvela, H. Grénman, K. Eränen, R. Sjöholm, M. Reunanen, and D.Y. Murzin, *Chemical Characterization of Lube Oils.* Energy & Fuels, 2013. **27**(1): p. 27-34.

45. M.C. Garry and J. Bowman, *FT-IR Analysis of Used Lubricating Oils –General Considerations*, in *Thermo Fisher Scientific Inc*. 2007, Thermo Fisher Scientific Inc.

46. M. T. Devlin, T. Dvorsak, K. Garelick, J. M. Guevremont, G. Guinther, K. Hux, J. T. Loper, and R. Sheets, *Effect of Fluid Aging on ZDDP Tribofilm Formation and Tribofilm Properties.* International Automotive Forum & SAE-China Congress, 2010.

47. A.M. Barnes, K.D. Bartle, and V.A. Thibon, *A review of zinc dialkyldithiophosphates (ZDDPS): characterisation and role in the lubricating oil.* Tribology International, 2001. **34**(6): p. 389-395.

48. R.C. Coy and R.B. Jones, *The Thermal Degradation and EP Performance of Zinc Dialkyldithiophosphate Additives in White Oil.* ASLE Transactions, 1981. **24**(1): p. 77-90.

49. Zh. Yin, M. Kasrai, M. Fuller, G.M. Bancroft, K. Fyfe, and K.H. Tan, *Application of soft X-ray absorption spectroscopy in chemical characterization of antiwear films generated by ZDDP Part I: the effects of physical parameters.* Wear, 1997. **202**(2): p. 172-191.

50. P.A. Willermet, D.P. Dailey, R.O. Carter Iii, P.J. Schmitz, and W. Zhu, *Mechanism of formation of antiwear films from zinc dialkyldithiophosphates.* Tribology International, 1995. **28**(3): p. 177-187.

51. P. Ramkumar, L. Wang, T. J. Harvey, R. J. K. Wood, K. Nelson, E. Yamaguchi, J.J. Harrison, and H.E.G. Powrie, *The Effect of Diesel Engine Oil Contamination on Friction and Wear*, in *World tribology congress, 3rd 2005; WTC2005-63854*. 2005.

52. S. Berkani, F. Dassenoy, J.M. Martin, H. Cardon, G. Montagnac, and B. Reynard, *Structural Changes in Tribo-Stressed Zinc Polyphosphates.* Tribology Letters, 2013. **51**: p. 489-498.

53. R. Penchaliah, T J. Harvey, R J K. Wood, K. Nelson, and H E G. Powrie, *The effects of diesel contaminants on tribological performance on sliding steel on steel contacts.* Engineering Tribology, 2011. **225**(8).

54. W. Cadman and J. Johnson, *The Study of the Effect of Exhaust Gas Recirculation on Engine Wear in a Heavy-Duty Diesel Engine Using Analytical Ferrography.* SAE Technical Paper 860378, 1986: p. 24.

Highlights of this papers:

- A lab-based artificial ageing technique were used to age the engine oil which is a more realistic condition.
- The high wear observed in the presence of carbon black (CB) in oil is not solely due to abrasion.
- It is found that the parasitic consumption of the additives by CB in the engine oil during the ageing process (additive adsorption) has a significant effect on wear of the components.
- Additive adsorption mechanism has a higher impact on producing high wear than abrasion by the CB particles.
- It is also found that the contaminants and ageing conditions can affect on the performance of engine oil. This is found to be dependent on the type of contaminants and ageing duration.