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The Effect of Temperature and Asphaltene Content on the Lubricating Properties of Fuel Oils

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Abstract: During coal-based power generation, fuel oil is used to assist with ignition of pulverised coal. Fuel oil passes through several pieces of equipment on its way to the burner section of the boiler. In this article the focus is on the lubricity behaviour of three representative fuel oil types and on the potential blocking of filters and nozzles caused by the presence of unwanted components in these fuel oils. The high frequency reciprocating rig (HFRR) (ISO 12156-1) was used to determine the lubricity of these fuel oils at different temperatures. Results indicate that the presence of asphaltenes (components of heavy fuel oils with complex aromatic structures) changes the viscosities of fuel oils, which, in turn affect their lubricity behaviour. Medium wax-blend fuel oil (MFO) containing high molecular weight paraffins (wax), low concentrations of asphaltenes and solid particles caused less friction and wear (with coefficient of friction (COF) values below 0.1) and good high temperature performance. Crude-derived heavy fuel oil (HFO), containing high concentrations of asphaltenes and solid particles caused very high coefficients of friction (COF peaks above 0.3) and severe abrasive wear at high temperatures. Although the third fuel oil tested was a light cycle oil (LFO) and did not contain any asphaltenes, results indicated a sensitivity to oxidation, increasing with temperature, which can have an adverse effect on in situ performance.

Keywords: asphaltenes; precipitation; lubricity; friction; wear

1. Introduction

In the recent past, several users of fuel oils have been experiencing problems such as blockages in fuel oil filters and injector nozzles, increased wear and failures of pumps and, in some cases, decreased calorific efficiency of combustion. These problems appear to be linked to the chemical and physical properties of the components of the fuel oil. The most prominent problematic part of the composition appears to be the presence of asphaltenes [1].

Asphaltenes are components of heavy fuel oil with complex aromatic structures containing heteroatoms (N, O, S) and metals (V, Fe, Ni) [2,3]. They are major precursors of sludge or sediments and are known to contribute to coke and sludge formation in refineries in addition to catalyst deactivation during processing [4], ([5] p. 1). Precipitation and deposition of asphaltenes occur during normal refining operations which means that it is hardly avoidable (e.g., during the production of heavy fuel oil, lighter hydrocarbons or paraffinic oils are used as diluent to reduce the viscosity of crude oil). The use of lighter hydrocarbons or paraffinic oils can trigger asphaltene precipitation in tubes, pipelines and on exposed surfaces, as asphaltenes dissolve in light aromatic hydrocarbons and precipitate in low carbon number n-alkane solvents [4,6]. These problems and their causes need to be confirmed and addressed in a way that will help to improve current fuel oil requirements for industrial use.

The aim of this investigation was to determine the lubricating properties of fuel oils by focusing on their friction and wear capabilities taking into account the presence of particulate matter and of asphaltenes. The objective of this investigation was therefore to perform friction and wear tests on the filtered and unfiltered fuel oils at different

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temperatures using a HFRR tribometer, which has become an important industry standard test for diesel fuel lubricity ([7] p. 914), [8].

Severely loaded systems such as nozzles, injectors or pumps require lubricants with high lubricity to avoid wear problems [9]. Poor lubrication is indicated by a high coefficient of friction (COF) with significant metal-to-metal contact taking place in the boundary lubrication regime resulting in wear. Significant friction occurs when both contacting surfaces are without chemical films and adsorbed components [8]. Poor lubricants have a potential for causing premature wear which leads to high repair costs and failure of pumps [10]. Friction reduction and wear control are therefore of particular importance for economic reasons and long-term reliability of equipment [11] (p. 4).

Fuel oils comprise a range of liquid combustibles, mainly hydrocarbons, which are obtained either as distillates in the working up of crude oil or as residues after the lighter fractions have been removed [12] (p. 120). Fuel oils are used for industrial and marine operations because fuel oils are cheaper than diesel [13]. Burner shut-downs can be caused by contamination of fuel, fuel degradation and poor fuel quality. Fuel stability, thermal stability, viscosity and fuel cleanliness affect flow and the nozzle and filter clogging tendencies of the fuel in use [14]. The formation of particulate matter introduces problems related to blockages and wear resulting in expensive maintenance costs. Moreover, the solid particles associated with the heavy fuel oil's exhaust gases result in harmful effects on the environment and human health [13]. Abrasive contaminants in fuel and active chemical compounds intensify wear processes [15]. The maximum particulate contamination in middle distillate fuel oils is 25 (mg) m^{-3} by filtration according to the ASTM D6217-18 standard test method [16].

The ASTM D396 standard specification for fuel oils covers grades of fuel oil intended for use in fuel oil burning equipment. The specification classifies fuel oils into six grades numbered in order of increasing density and viscosity, with number six being the heaviest fuel oil and number one being the lightest fuel oil [14]. The fuel oils labelled no. 1, 2 and 3 are referred to as distillate fuels oils, whereas no. 4, 5 and 6 are referred to as residual fuel oils [17] (p. 336). Distillate fuel oil is lighter, thinner and better for a cold start when compared to residual fuel oil [18]. Straight run kerosene is a light distillate fuel oil, without further processing, which consists primarily of hydrocarbons in the C_{11}–C_{20} range [14]. Kerosene is intended for use in vaporising type burners due to its high volatility [18]. Fluid catalytic cracking (FCC) reactor units in a refinery convert heavy fuel oils into lighter products. Light cycle oil (LCO), a distillate fuel oil, is a by-product of the FCC reactor. LCO can be used as a blending component in heavy fuel oils for viscosity adjustments in order to reduce the final viscosity [19,20]. Diesel fuel oil (No. 2 heating oil) is generally a blend of straight-run product, LCO and hydrocracked products. Diesel fuel oil, a heavier distillate fuel oil than kerosene, contains approximately 64% aliphatic hydrocarbons, 35% aromatic hydrocarbons and 1–2% olefinic hydrocarbons [21]. Diesel fuel oil, used in commercial-industrial burners and in domestic burners, is produced for atomizing type burners [22]. The distinction between diesel fuel used in internal combustion engines (IC) for vehicles and diesel fuel used as heating fuel oil is its sulphur content. Diesel for vehicles, must have a cetane number higher than diesel fuel oil (No. 2 heating oil), a key characteristic for diesel engines, which affects how smoothly the fuel burns, however, it is irrelevant for heating fuel oils [14,23]. Residual fuel oil is the residue of crude oil distillate that is still flowable under standard temperature and pressure (25 °C and 101.325 kPa). Waste oils from other sources are often added to residual fuel oils. A distinct composition cannot be determined for residual fuel oils, because of their complexity and variability. Residual fuel oils have complex composition and impurities compared with distillate fuel oils [13,21].

Properties of heavy (residual) fuel oils show that the polar fractions, including asphaltenes, are likely to be irreversibly adsorbed onto a metal surface and are less resistant to oxidation as compared to paraffins because of their polarity [3,4], ([24] p. 38).

Asphaltenes play a major role in the high viscosity behaviour of the heavy fuel oils [3]. Properties of heavy fuel oils show that the polar fractions, more specifically asphaltenes, have been identified as the cause of their unique rheological behaviour [25]. Asphaltenes reduce the economic value of crude oil. As asphaltene content increases from 0% to 40%, the crude oil's viscosity and density increase drastically and the crude oil changes colour from clear to dark brown [26]. Viscosity depends directly and exponentially on asphaltene content. Experimental results from a study, where asphaltenes were removed from heavy fuel oils and then added back to the maltenes (saturates, aromatics and resins), indicate that viscosity of the reconstituted heavy fuel oil samples increases exponentially as the asphaltene content increases at constant temperature [3]. Distillate fuel oils can be used as a blending component in heavy fuel oil for viscosity adjustments in order to reduce the final viscosity of heavy fuel oil [20].

This investigation focused on fuel oil used in industrial burners in order to obtain a fuel oil benchmark to quantify lubricity of fuel oils in a similar way to other liquid products, for which standardised lubricity specifications exist. According to ASTM D396-18a, the maximum wear scar diameter (WSD) for distillate fuel oils is 520 µm, however the standard does not report on WSD specifications for residual fuel oils [27]. As mentioned earlier, the aim of this investigation was thus to determine the lubricating properties of fuel oils used in power generation by focusing on their friction and wear capabilities, whilst also taking into consideration the effect of the presence of asphaltenes in fuel oils over a range of temperatures for filtered and unfiltered fuel oil samples.

The three representative fuel oil samples used in this study were provided by Sasol (a local refiner of crude oils and producer of synthetic fuels) namely:

(i) A light cycle oil (LFO), which is a distillate fuel oil not containing asphaltenes;
(ii) A medium wax-blend fuel oil (MFO) containing high molecular weight paraffin (wax), low concentration of asphaltenes and solid particles;
(iii) A crude-derived heavy fuel oil (HFO) containing high concentrations of asphaltenes and solid particles.

2. Materials and Methods

Experiments were designed to measure physical and chemical properties, followed by friction and wear testing under various temperatures. Triplicate test runs were performed for most experiments to ensure consistent results.

2.1. Elemental Analysis

In order to characterize the elemental composition of the fuel oil, analysis was performed using ICP-OES (Inductively coupled plasma-optical emission spectrometry) using a Spectro Arcos machine supplied by the Materials Division of Ametek Inc., Berwyn, PA, USA. The elemental analysis was performed on the unfiltered and filtered fuel oil samples. The preparation method used for the analysis was the wet-ashing procedure [28]. A mass of 2 g of fuel oil sample was weighed in a platinum crucible. 2 mL of sulphuric acid (98%) was slowly added into the crucible and mixed with the fuel oil. The sample was incinerated at 550 °C for 2 h. Once the crucible had cooled down, the ash was dissolved in 1.5 mL of nitric acid and then diluted with 40 g of distilled water [28].

2.2. Precipitation of Asphaltenes

Asphaltene fractions and solid particles were removed by precipitation from the three fuel oils by treatment with a non-polar hydrocarbon solvent (n-heptane) [2]. A sample of 10 mL of fuel oil was mixed with 400 mL of 99% purity n-heptane. The mixture (fuel oil + n-heptane) was stirred for 24 h at 25 °C with a stirrer speed of 250 rpm and then allowed to settle for approximately 3 h at 25 °C [5] (p. 1). It was ensured that the beaker is covered using a watch glass throughout the stirring and settling period to reduce the rate of evaporation of n-heptane. Although LFO does not contain asphaltenes (because LFO is a distillate fuel oil), the solid particles in LFO were removed as the asphaltenes filtration procedure does not only remove asphaltenes but also removes solid particles.

The precipitated asphaltenes (if any) as well as solid particles were separated from the remaining fuel oil and solvent mixture by vacuum filtration through two 0.2-micron nylon membrane filters. For the vacuum filtration setup (used to separate the solid particles and/or precipitated asphaltenes from the maltenes and n-heptane mixture) the 0.2-micron nylon membrane filters were placed in an oven at 110 °C for 10 min to eliminate moisture. The filter papers were then weighed individually and placed back in the filtration apparatus. The pump was connected to the Büchner flask and switched on to start the filtration process, as shown in Figure 1 below.

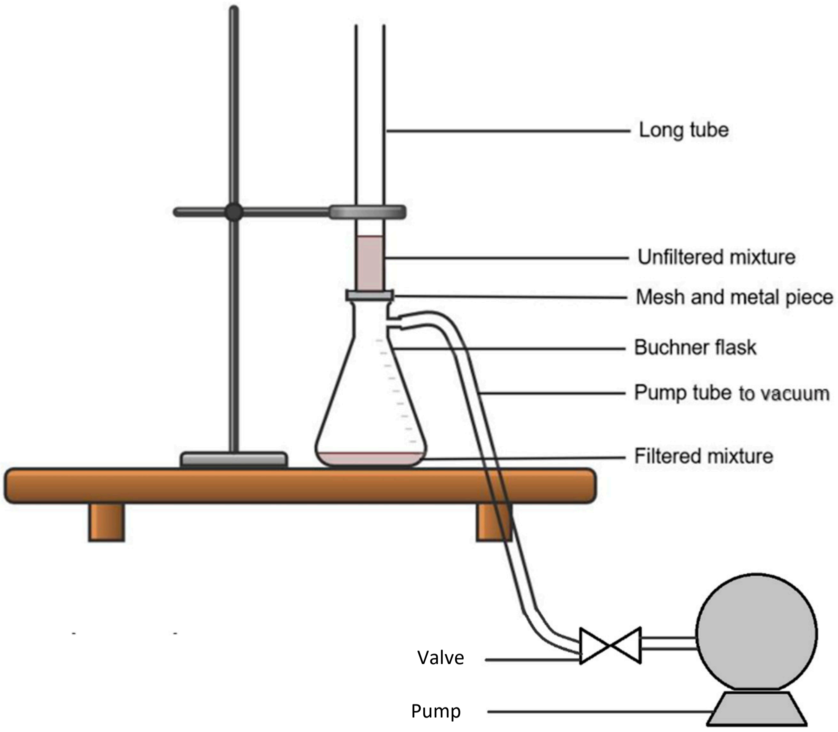


Figure 1. Diagram of the asphaltene vacuum filtration setup.

Once the fuel oil and n-heptane mixture was poured into the long tube, the asphaltenes and solid particles were subjected to vacuum filtration at room temperature for approximately 24 h for LFO and HFO, and for approximately 36 h for MFO (MFO has waxy precipitants which take longer to separate from the asphaltenes). It was ensured that the vacuum filtration remained on for 24 h for LFO and HFO and 36 hrs for MFO even though the filtration may have been completed earlier—this aids in the separation of the maltenes and the n-heptane (evaporation of n-heptane). After filtration, the filter papers were dried in an oven at 110 °C (higher than the boiling point of n-heptane) for 15 min to make sure that the asphaltenes and filter papers were completely dry. The filter papers were removed from the oven to cool off and then weighed. The filtered mixture was poured into a container and left in a desiccator for 24 h, ensuring that the mixture container was open to allow for evaporation of the remaining n-heptane. After 24 h, the container was closed for storage until required for the HFRR friction and wear testing.

While establishing the vacuum filtration procedure, the filters used were 0.8 micron nylon membrane filters. It was found that this filter size was too big since visual inspection of "filtered fuel oil" showed that particles were still present. This is an indication that most of the asphaltenes particles are below 0.8 micron and therefore a smaller filter size was required. The 0.8 micron nylon membrane filters were replaced with 0.2 micron nylon membrane filters. It was also found that, after filtration of the fuel oil, the Büchner flask should be heated to 50 °C in order to decrease the viscosity and therefore remove most of the filtered fuel oil for storage and sebsequent use in friction and wear testing. Heating of the filtered fuel oils resulted in increased viscosity of the filtered MFO, which contains waxes, once the sample had cooled down. The filtrates were removed from the Büchner flask without heating to ensure that the physical properties would remain the same.

2.3. Lubricity Tests

The HFRR produces results via measurements of the continuous friction force, the contact resistance (film) and the test fluid temperature values. The film measurement results are a qualitative indicator of film formation and cannot be used to deduce the real area of contact. Therefore, the results are not as significant as the COF and inconsistency of results are expected [29]. The components of the machinery comprise a mechanical unit, control unit and a computer. The control unit is connected to a computer for data logging, graphical representation of test parameters and results storage [8]. Figure 2 shows the schematic of the HFRR machine.

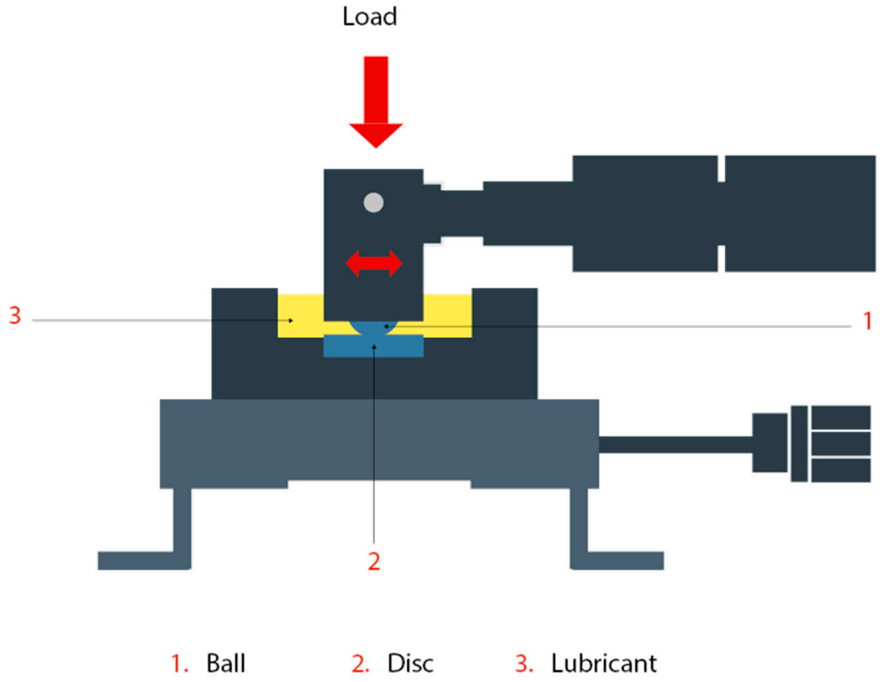


Figure 2. Schematic of the HFRR machine by PCS Instruments, Reprinted with permission from PCS Instruments.

Friction and wear tests were performed according to ISO 12156-1 on the HFRR under atmospheric air for filtered and unfiltered fuel oil samples. In order to report on the effect of temperature, the HFRR tests were performed at different temperatures (25, 60, 100 and 115 °C). Triplicate test runs were performed to ensure consistent results. A summary of the HFRR test conditions is shown in Table 1.

Table 1. HFRR test conditions.

Parameter	Value
Stroke length, mm	1 ± 0.02
Frequency, Hz	50 ± 1
Humidity, % (RH)	50 ± 5 (Air)
Fluid temperature, °C	115 ± 2, 100 ± 2, 60 ± 2, 25 ± 2
Load, g	200 ± 1
Test duration, min	75 ± 0.1
Fluid volume, mL	2 ± 0.2
Reservoir surface area, mm^2	600 ± 100

The lubricity tests were chosen to be performed on filtered and unfiltered fuel oils performed at 25, 60, 100 and 115 °C. The 115 °C HFRR runs were performed simply to confirm that the investigation should not go beyond the normal boiling point of water. Expected evaporation takes place at 115 °C because the fuel oils contain certain amounts of volatiles. The results at 115 °C do not contribute to understanding of the temperature effects on fuel oils, which is seen by the change in trend at 115 °C in the HFRR results below. The fuel oils were filtered to investigate how the fuel oils would be performing without the presence of solid particles and/or asphaltenes. This helps to determine the impact of the solid particles and/or asphaltenes on the lubricity of fuel oils. Comparison of the filtered and unfiltered fuel oil lubricity results will give an indication of the effect of the solid particles and/or asphaltenes on the lubricity of the different fuel oils.

The 50% relative humidity (RH) choice under air atmosphere was selected because the humidity is within the acceptable laboratory air conditions for a standard lubricity test according to ISO 12156-1.

A humidifier was used to control the relative humidity of the HFRR chamber to 50% (RH) under atmospheric air. The humidity was monitored throughout the HFRR test using a Sensirion SHT2x humidity sensor since the chamber is not a completely closed system as some gaseous emissions leave the chamber throughout the test.

Air supply passes through moisture and particle filters. The wet air from the bubbler and dry air from the dryer mix to give the required relative humidity in the HFRR chamber. The flow rates of the bubbler and dryer were controlled by adjusting the needle valves throughout the test as shown in Figure 3.

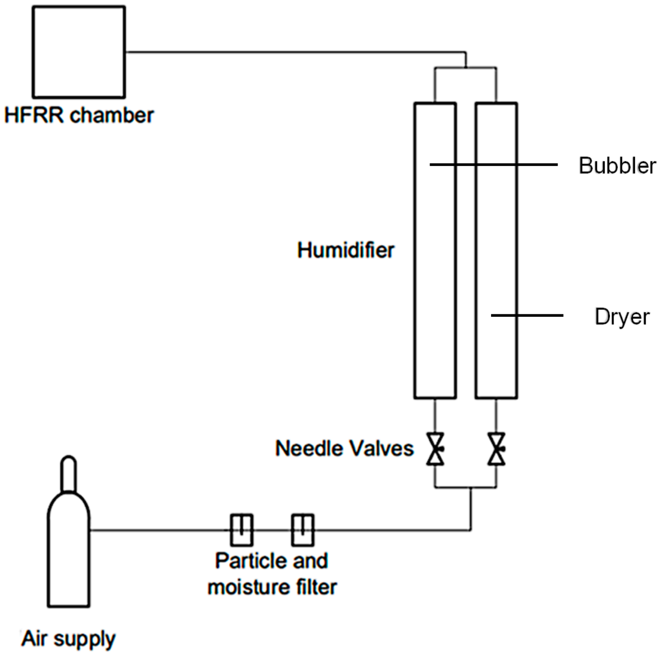


Figure 3. Humidifier assembly.

3. Results

3.1. Viscosity Measurements

An Anton Paar SVM 3000 Stabinger (Graz, Austria) viscometer was used to measure the dynamic viscosity of unfiltered fuel oils at different temperatures. The dynamic viscosity of the unfiltered fuel oils at different temperatures is shown in Figure 4. The results show that the viscosities of the fuel oils tested decrease exponentially with increasing temperature. The absence of asphaltenes in LFO results in lower viscosity measurements and a gentle gradient for viscosity versus temperature graph as compared with MFO and HFO.

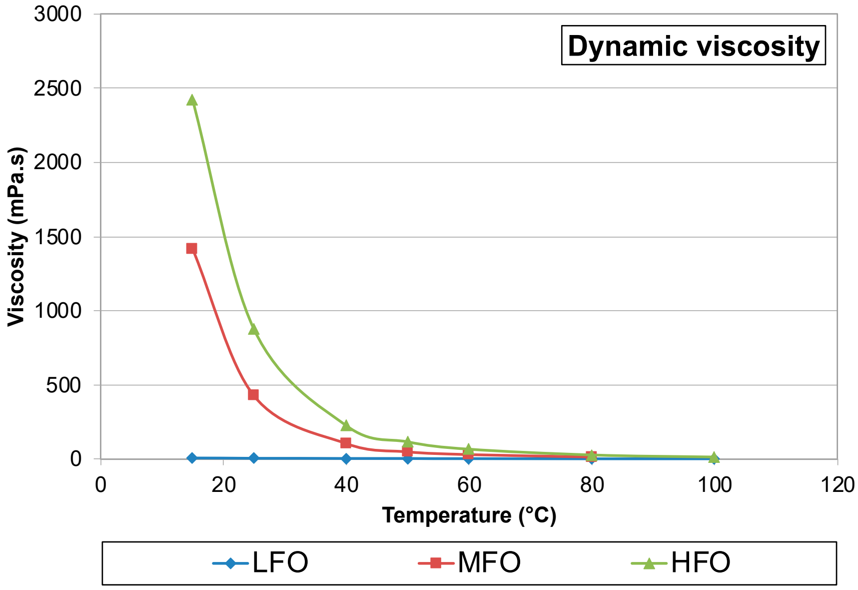


Figure 4. Dynamic viscosity of unfiltered fuel oils at different temperatures.

3.2. Water Content Measurements

Water content measurements were performed using a Metrohm 870 KF Titrino+. The one-component volumetric KF titration was used for water content determination [30]. The water content results for LFO, MFO and HFO were 0.1%, 0.12% and 0.13%, respectively. Results show that the water content increases with (assumed) increasing asphaltene content. MFO and HFO are polar fuel oils containing asphaltenes. Water content contributes to the formation of a protective layer (iron oxide) and therefore improves lubrication. Although MFO and HFO have more free water, the polar species in MFO and HFO are preferentially adsorbed which prevents the formation of an oxide layer. For LFO, the low concentration of polar compounds and reactive species tend to form an oxide layer on the metallic surfaces [9].

3.3. Elemental Analysis

From the ICP-OES analyses for unfiltered fuel oils shown in Table 2, HFO has the highest concentration of asphaltenes and solid particles compared with MFO and LFO. The asphaltene concentration is shown by the high concentration of vanadium, nickel and iron (metals found in asphaltenes) in HFO compared with MFO since LFO does not contain asphaltenes as LFO is a distillate fuel oil. The high metal content in LFO may be because the catalytic reactor feed was not pre-treated resulting in a low-quality light cycle oil with high concentration of metal but not asphaltenes. The silica concentration in LFO is higher compared to MFO and HFO because light cycle oils pass through a catalytic reactor which uses silica as a catalyst. The fine silica particles remain in the LFO.

From the ICP analyses for filtered fuel oils shown in Table 3, the concentration of asphaltenes and solid parts have drastically decreased for LFO, MFO and HFO compared to the unfiltered ICP-OES results shown in Table 2. The abrasive particles in the fuel oils have been removed from the fuel oils, only fine particles remain in the fuel oil (<0.2 micron). The remaining asphaltenes in MFO and HFO, if any, are dispersed asphaltenes (<2 µm) [31].

Table 2. ICP-OES results for unfiltered fuel oils.

Sample	HFO (mg/kg)	MFO (mg/kg)	LFO (mg/kg)
V	14.7	4.94	2.15
Ni	10.5	2.37	1.61
Na	80.8	1.78	6.80
Fe	28.6	6.71	18.1
Mn	1.69	1.18	1.07
Mg	9.21	2.96	4.65
K	11.1	2.76	4.11
S	883	118	159
Cr	4.32	1.58	3.76
Ca	124	60.6	85.2
Al	216	2.37	1.79
P	18.6	-	-
Zn	9.77	2.57	3.04
Si	5.26	8.69	11.3

Table 3. ICP-OES for filtered fuel oils.

Sample	HFO (mg/kg)	MFO (mg/kg)	LFO (mg/kg)
V	2.82	1.26	0.219
Ni	1.60	0.709	0.310
Na	8.96	8.37	8.40
Fe	6.67	4.77	3.50
Mn	0.415	0.236	0.346
Mg	2.19	2.01	2.22
K	0.415	0.296	0.492
S	1.52	1.28	1.86
Cr	1.09	0.394	0.510
Ca	41.4	30.6	44.46
Al	1.42	0.768	0.601
P	0.138	0.887	0.237
Zn	1.05	0.788	1.04
Si	4.70	2.52	2.04

3.4. Asphaltene Content and Solid Particles Measurements

The concentration of asphaltenes and solid particles as measured via the filter cake increases in the order LFO, MFO and HFO. The concentration of asphaltenes and solid particles for LFO, MFO and HFO were 5.67 ± 1.71, 23.5 ± 0.125 and 48.7 ± 2.84 g $(L)^{-1}$. Figure 5 shows the filter cakes for the fuel oils. The filter papers were all the same size, namely 47 mm in diameter, as indicated in the first photograph.

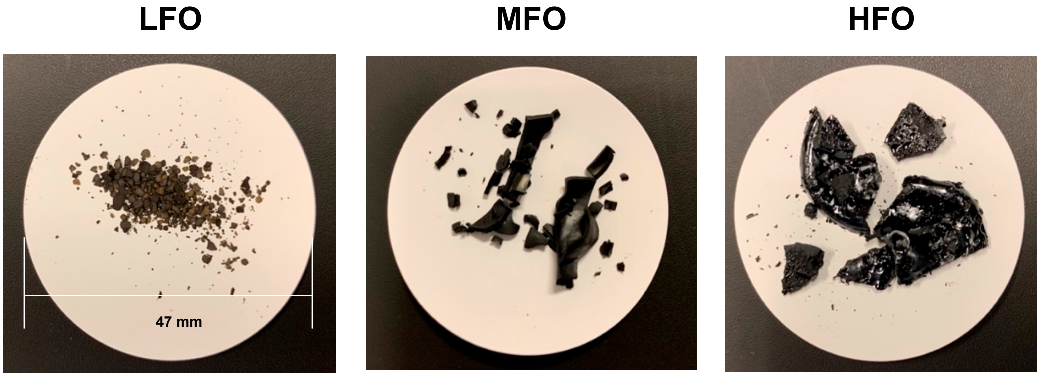


Figure 5. Precipitated asphaltenes and solid particles for the fuel oils.

3.5. Lubricity Tests

From the COF versus time graphs for unfiltered and filtered LFO shown in Figure 6, the COF of unfiltered and filtered LFO increases with the increase in temperature. Unfiltered and filtered LFO at 25 °C have the lowest COF throughout the test. This is a result of a viscosity-temperature relationship. At low temperatures the viscosity is higher, resulting in a thicker film. The thicker film allows for separation between the contacting surfaces [24] (p. 11). At 25 °C, the COF is drastically higher for filtered LFO when compared with unfiltered LFO. The removal of solid particles in filtered LFO also removes molecules with good lubricity resulting in increased COF when compared with unfiltered LFO [9].

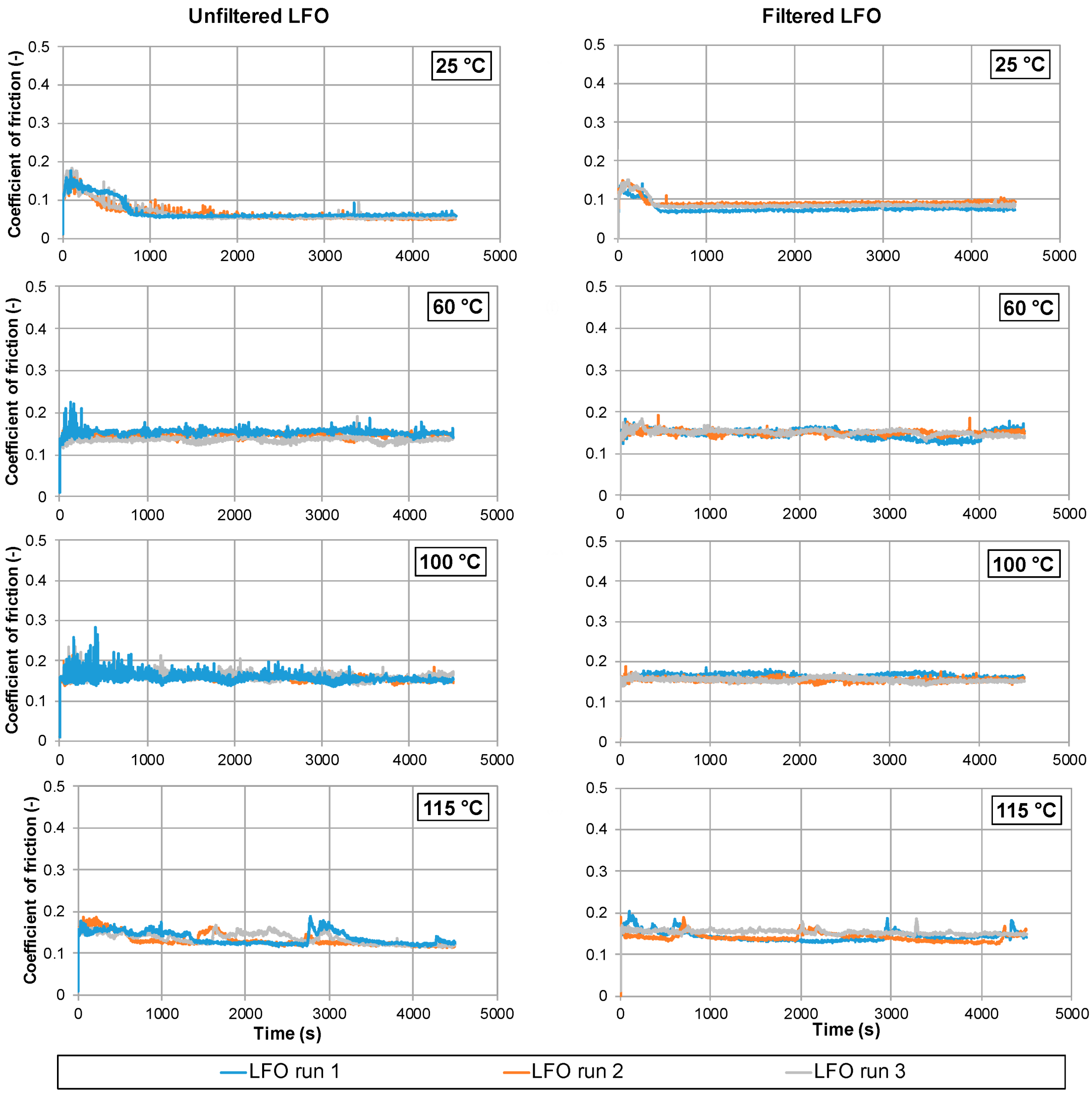


Figure 6. COF versus time graphs of unfiltered and filtered LFO for three runs at 50% RH.

Between 60 °C and 100 °C, the COF is similar for filtered and unfiltered LFO, although the roughness of the COF for unfiltered LFO is much more severe when compared with filtered LFO—especially at high temperatures. This is due to the solid particles in unfiltered LFO which interact with the surface, resulting in concentration of heat at the contacts resulting in a rougher COF profile [24] (p. 11). The presence of oxidation is also responsible for the COF instability of the filtered and unfiltered LFO. At 60 and 100 °C, the increased roughness of the COF for unfiltered LFO is due to the dynamic nature of the oxide formation in the presence of solid particles. This can be seen by reduced roughness of COF for filtered

LFO. Oxidation is predominant in LFO under oxygen atmosphere (50% RH) especially at high temperatures.

From the COF versus time graphs of unfiltered and filtered MFO shown in Figure 7, the increase in temperature for unfiltered and filtered MFO results in decreased stability of the COF. At 25 °C, the low temperature limits chemical wear taking place because there is minimal frictional heat present but as temperature increases, the protective layer is more likely to be rubbed away due to increased frictional heat resulting in the instability of COF [4], ([11] p. 359). There is minimal change in COF for filtered MFO and unfiltered MFO at different temperatures.

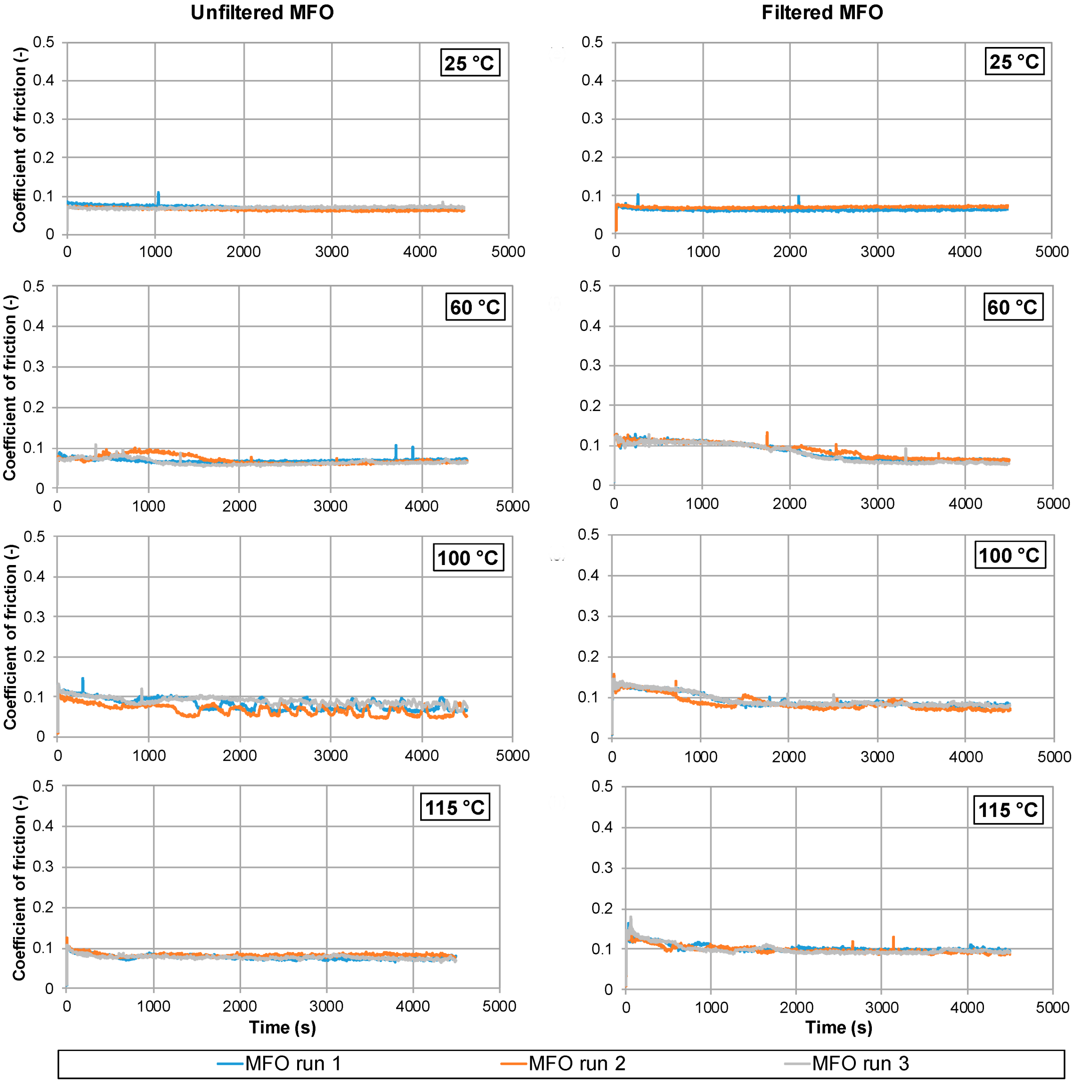


Figure 7. COF versus time graphs of unfiltered and filtered MFO for three runs at 50% RH.

Asphaltenes and some waxes were removed during the filtration process for MFO. Waxes have good lubricating properties and removal of some waxes and asphaltenes resulted in no apparent effect in COF when compared with unfiltered MFO. The asphaltenes are very polar compounds which adsorb on the metal surface resulting in formation of a protective layer. This results in similar COF values for unfiltered and filtered MFO with a smoother profile for filtered MFO due to removal of asphaltenes and solid particles.

From the COF versus time graphs of unfiltered and filtered HFO shown in Figure 8, the COF for filtered HFO and unfiltered HFO decreases between 25 and 60 °C. The lower COF at 25 °C is due to the high viscosity at low temperatures resulting in more power for HFO to be sheared. The power losses are higher, and more heat is generated resulting in increased heat of the contacting surfaces which leads to a higher COF at 25 °C than at 60 °C [24] (p. 11). At the lower temperatures (25 and 60 °C), there is more separation of the contacting surfaces due to the higher viscosity which results in a thick film when compared with the results at temperatures above 60 °C. The thick film ensures negligible interactions of the asphaltenes and solid particles in unfiltered HFO and the contacting surfaces.

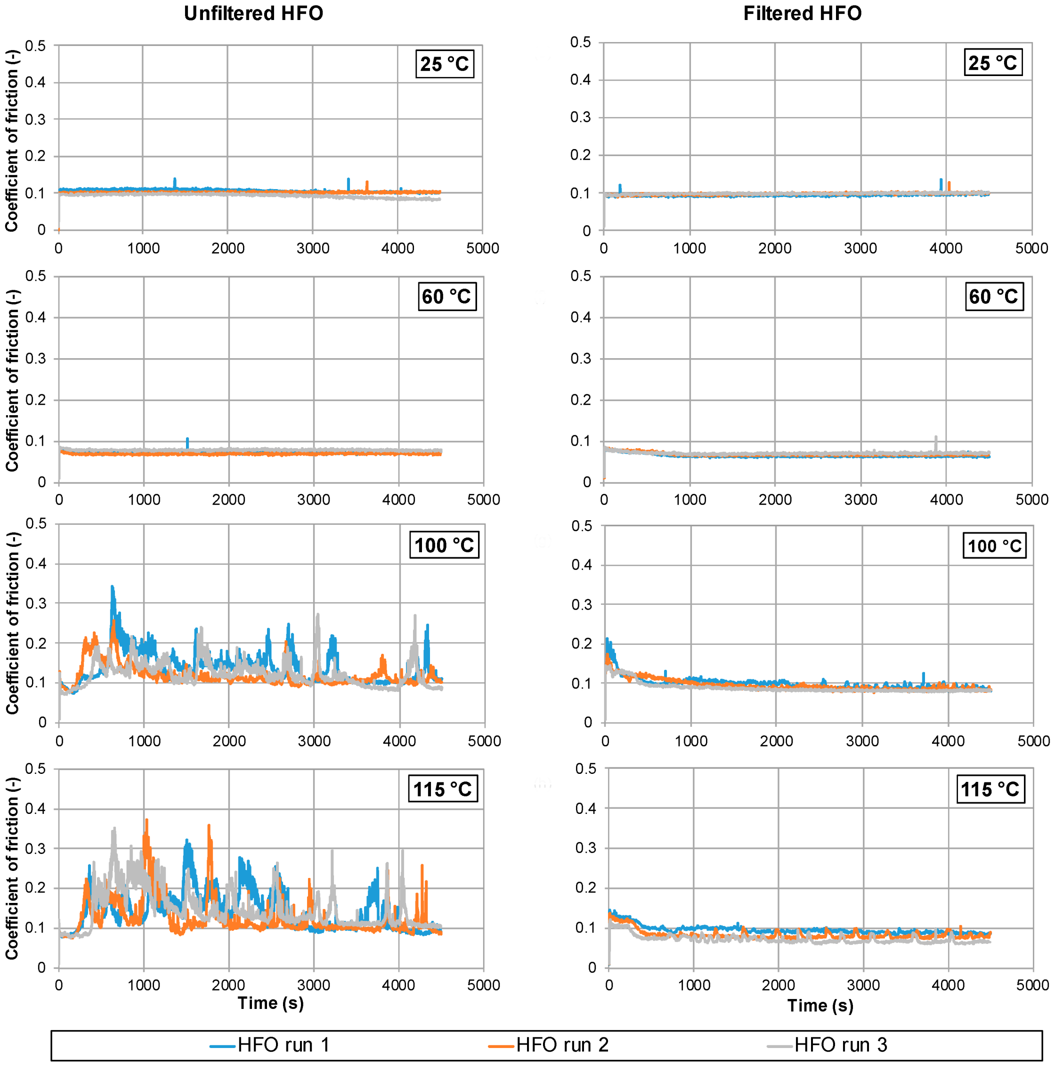


Figure 8. COF versus time graphs of unfiltered and filtered HFO for three runs at 50% RH.

At 100 °C, the COF values for unfiltered HFO fluctuate throughout the test with high COF peaks. The high and rough COF at 100 °C could be due to breakthrough of the fuel oil film—this will be confirmed by the wear results. Unfiltered HFO contains a high concentration of asphaltenes and solid particles. At high temperatures the effects of the asphaltenes and solid particles are most prominent due to the drastic decrease in viscosity and therefore the reduction in film thickness, resulting in more interactions between the asphaltenes and solid particles in unfiltered HFO and on interacting surfaces. The interactions lead to concentration of heat which increases the COF and results in a rougher COF profile [24] (p. 11). For filtered HFO under oxygen-rich atmosphere, the COF values are low (0.1) at 100 °C. The removal of abrasive asphaltenes and solid particles during filtration shows significant decrease in the COF and especially a much more even COF pattern over time.

3.6. Wear

The wear scar micrographs produced from the friction and wear tests are shown below with their respective complementary ratings (CR) and average corrected wear scar diameters ($WS_{1.4}$). $WS_{1.4}$ is a calculated value of wear scar diameter to the standardised water vapour pressure of 1.4 kPa. The equation used to calculate the $WS_{1.4}$ is Equation (1) according to the ISO 12156-1 test method [32].

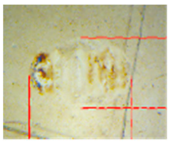
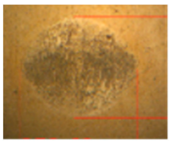
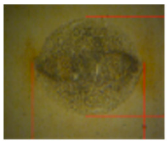
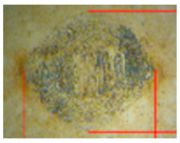
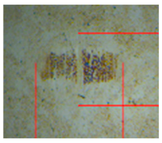
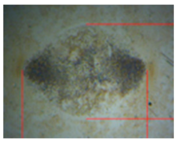
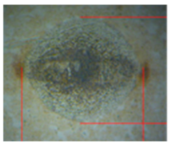
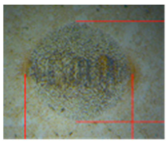
$$WS_{1.4} = MSWD + HCF(1.4 - AVP) \tag{1}$$

where HCF = 60, $MSWD$ is the uncorrected wear scar diameter in µm and AVP is the mean absolute vapour pressure (in kPa) during the test. According to ISO 12156-1, a humidity correction factor (HCF) of 60 µm $(\text{kPa})^{-1}$ is proposed for all fuels as a correction of the vapour pressure, regardless of their composition [9].

The CR helps to identify different wear mechanisms which lead to different visual appearances on the ball. The CR is based on a 6-graded visual rating scale method with 1 being excellent (full) lubrication and 6 being no lubrication with distinct wear marks inside the contact [33]. Note that the wear scar micrographs are not to scale.

For unfiltered LFO, the CR decreases from 25 to 60 °C and increases from 60 to 100 °C. From the wear scars for filtered and unfiltered LFO shown in Table 4, at high temperatures, slight abrasion occurs due to a decrease in the viscosity which results in reduction in the film thickness and therefore less separation between the solid particles and metal surfaces for the unfiltered LFO [24] (p. 11). As the temperature increases for unfiltered LFO, the degree of oxidation increases. This is seen by the darkening of the wear scar due to increased oxidation which causes oxide formation on the contact surface [33].

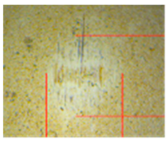
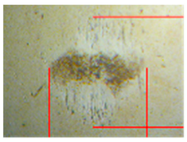
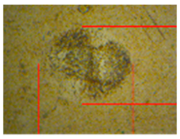
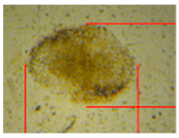
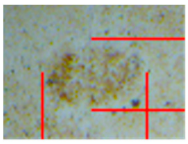
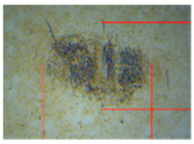
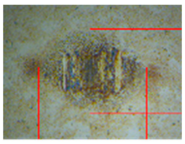
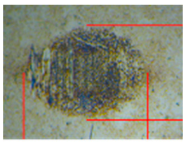
Table 4. Wear scars for filtered and unfiltered LFO at different temperatures at 50% RH.

	25 °C	**60 °C**	**100 °C**	**115 °C**
Unfiltered LFO				
CR $WS_{1.4}$ (µm)	3 191	2 360	3 364	4 295
Filtered LFO				
CR $WS_{1.4}$ (µm)	3 145	2 348	2 375	2 307

For filtered LFO, the CR is the highest at 25 °C and stays constant between 60 and 100 °C at a CR of 2. Oxidative wear is the lowest at 25 °C for filtered and unfiltered LFO because of the low temperature. Oxidative wear occurs at high temperatures [11] (p. 359). There is no abrasion for filtered LFO. The wear scars for filtered LFO and unfiltered LFO look similar with filtered LFO having less abrasive wear due to the removal of solid particles. The solid particles interact with the surfaces which results in increase in CR and more wear. For unfiltered and filtered LFO, increase in temperature results in an increase in $WS_{1.4}$. The increase in $WS_{1.4}$ for LFO is due to the decrease in viscosity with increasing temperature which results in less resistance to shear and decrease in film thickness. This causes the ball and disk to move closer together resulting in an increased $WS_{1.4}$ [24] (p. 11). At 25 °C, filtered LFO has a lower $WS_{1.4}$ when compared with unfiltered LFO. For 60 to 100 °C, there is minimal change in $WS_{1.4}$ with increasing temperature.

For unfiltered MFO, the CR stays constant between 25 and 60 °C at a CR of 3, then decreases from 60 °C to 100 °C. From the wear scars for filtered and unfiltered MFO shown in Table 5, the minimal change in the CR correlates with the minimal change in the COF with increasing temperature. As the temperature increases, the degree of oxidation on the wear scar increases resulting in the formation of a protective layer and therefore a decrease in abrasive wear [34]. This is seen by the darkening of the wear scar and less visible scratch lines with increasing temperature [33]. There is more oxidative wear present in filtered MFO when compared with unfiltered MFO with increasing temperature. For unfiltered MFO, the increase in temperature results in minimal change in the $WS_{1.4}$.

Table 5. Wear scars for filtered and unfiltered MFO at different temperatures at 50% RH.

	25 °C	**60 °C**	**100 °C**	**115 °C**
Unfiltered MFO				
CR	3	3	2	2
$WS_{1.4}$ (μm)	177	191	185	184
Filtered MFO				
CR	3	2	4	4
$WS_{1.4}$ (μm)	85	206	188	175

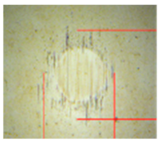
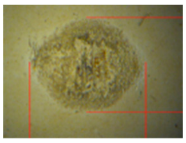
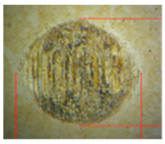
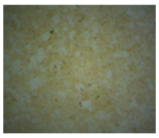
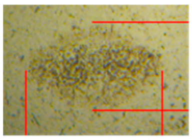
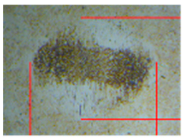
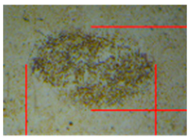
For filtered MFO, the increase in temperature results in an increase in abrasive wear and oxidative wear. The CR slightly decreases between 25 and 60 °C and increases between 60 and 100 °C at a CR of 4. For filtered MFO, there is an increase in $WS_{1.4}$ between 25 and 60 °C, although there is minimal change between 60 and 100 °C.

Filtered MFO shows abrasive wear at high temperatures (100 °C). The removal of some waxes during the filtration of asphaltenes resulted in more wear at high temperatures. The heavy fractions of the MFO, waxes and asphaltenes, play an important role in rheological behaviour of fuel oils [35]. The presence of waxes can modify asphaltene behaviour, accelerate the dissolution of asphaltenes and modify their stability. This means that the transition of asphaltenes to liquid form is accelerated, resulting in much higher viscosity of unfiltered MFO when compared with filtered MFO. This results in better separation between the metal surfaces at 100 °C and therefore less wear taking place.

At 25 °C, unfiltered MFO has a higher $WS_{1.4}$ when compared with filtered MFO. For 60 to 100 °C, there is minimal change in $WS_{1.4}$ for unfiltered MFO and filtered MFO. This correlates with the COF results shown in Figure 7.

From the wear scars for filtered and unfiltered HFO shown in Table 6, the CR and abrasive wear decrease for unfiltered HFO as the temperature increases from 25 to 60 °C, although the CR increases between 60 °C to 100 °C. The high abrasive wear at 25 °C is due to the high viscosity at low temperatures resulting in more power for HFO to be sheared. The power losses are higher and more heat is generated, resulting in increased heat of the contacting surfaces which leads to more wear [24] (p. 11). As temperature increases between 60 and 100 °C, abrasive wear increases due to decrease in viscosity resulting in a thinner film thickness which leads to abrasive particles of asphaltenes and solid particles interacting with the metal surfaces. The high concentration of asphaltenes in HFO results in asphaltene adsorption at the metal surface because of the very polar compounds in asphaltenes. The lower temperature (60 °C) limits chemical wear taking place because there is minimal frictional heat present but as temperature increases the protective layer is more likely to be rubbed away due to increased frictional heat resulting in increased wear [4], ([11] p. 359). For unfiltered HFO at 100 °C severe abrasive wear is present. The CR is not a 6 which is defined as no lubrication; therefore, we can conclude that unfiltered HFO at 100 °C does not result in breakthrough but instead results in severe wear.

Table 6. Wear scars for filtered and unfiltered HFO at different temperatures at 50% RH.

	25 °C	**60 °C**	**100 °C**	**115 °C**
Unfiltered HFO				
CR	6	3	4	5
$WS_{1.4}$ (µm)	217	222	343	431
Filtered HFO				
CR	-	3	3	3
$WS_{1.4}$ (µm)	No wear scar	137	201	168

Filtered HFO shows no wear scar at 25 °C; the viscosity is high, which results in a thick film capable of complete separation of the two contacting surfaces. As the temperature increases from 60 to 100 °C for filtered HFO, the CR remains constant. The removal of asphaltenes for filtered HFO results in no abrasive wear present. Oxidative wear becomes the dominant wear process which increases with increasing temperature.

The CR for filtered HFO is much lower than unfiltered HFO at different temperatures. This is due to the removal of asphaltenes and solid particles which are highly abrasive and play a major role in the viscosity of the fuel oil. At 25 °C, unfiltered HFO has a $WS_{1.4}$ of around 200 µm, whereas filtered HFO has no wear scar. For 60 to 100 °C, unfiltered HFO has a higher $WS_{1.4}$ when compared with filtered HFO.

4. Discussion

The effect of temperature and asphaltene content on friction and wear behaviour were investigated in this study. Lubricity tests were performed on filtered and unfiltered fuel oils. The following conclusions may be drawn:

- LFO with no asphaltenes (solid particles only) has little impact on the COF and wear from 60 to 100 °C. The trends for COF and for wear are similar for both filtered and unfiltered LFO. The solid particles affect the roughness of the COF, minimal change in the $WS_{1.4}$ and slight abrasive wear due to the presence of metals and silica in the solid particles. The removal of solid particles results in minimal change in COF except at 25 °C where the unfiltered LFO has a drastic reduction in COF when compared with filtered LFO. The removal of solid particles in filtered fuel oils also removes molecules with good lubricity resulting in increased COF when compared with unfiltered LFO.
- MFO containing high molecular weight paraffin (wax), low concentration of asphaltenes and solid particles produces a stable fuel oil. MFO performs better with asphaltenes present because the wax stabilizes the asphaltenes resulting in the dissolution of asphaltenes at an accelerated rate. The effect of this is good high temperature performance (less friction and wear at high temperatures). For MFO, the removal of asphaltenes results in minimal change in COF and minimal change in $WS_{1.4}$ from 60 to 100 °C. Due to the presence of waxes in MFO, the wear results for MFO do

not follow the typical trend where the increase in temperature usually results in an increase in wear. For MFO, the removal of asphaltenes and solid particles resulted in a decrease in wear at low temperatures and an increase in wear at high temperatures.

- HFO containing high concentrations of asphaltenes and solid particles results in very high COF values and severe abrasive wear at high temperatures. At low and moderate temperatures, unfiltered HFO performs comparable to filtered HFO, whereas at high temperatures COF, abrasive wear and $WS_{1.4}$ drastically increase when compared with filtered HFO. Overall HFO performs better in the absence of asphaltenes and solid particles due to their abrasive nature—particularly at high temperatures.

5. Conclusions and Recommendations

Filtration of HFO should be performed before use for better performance because filtered HFO results in better lubrication due to removal of abrasive particles resulting in reduced friction and wear and to avoid sediment deposition. Filtration of LFO and MFO is not required before use. Unfiltered LFO and MFO have good lubricating properties and much less particles when compared with HFO. Filtering LFO results in minimal change in lubrication and filtered MFO results in worse lubrication when compared with unfiltered MFO due to the removal of waxes which have good lubricating properties. Fuel oils at lower temperatures protect equipment from premature wear and breakdown of equipment because there is less concentration of heat on the metal surfaces in comparison with what happens at higher temperatures.

Two perfectly stable fuel oils can be incompatible resulting in atmospheric sludge precipitation when mixed. In addition, two fuels may be compatible at some mixing ratios and not compatible at other mixing ratios, or two fuel oils can be compatible or incompatible over the entire mixing range. LFO could possibly be mixed with either MFO or HFO to reduce the viscosity because the main use of LCO is as a blending component in heavy fuel oils for viscosity adjustments in order to reduce the final viscosity of heavy fuel oils. This should be confirmed. Dispersants can be used to control the compatibility problems which could possibly arise [17] (p. 347).

Fuel oils at lower temperatures protect the equipment from premature wear and breakdown of equipment because there is less concentration of heat on the metal surfaces than at higher temperatures. Pumping unfiltered HFO and unfiltered MFO at lower temperatures may result in a much longer pumping period and require more power for the fuel oil to reach the burner section due to high viscosity of HFO and MFO as a result of the presence of asphaltenes. LFO can be pumped to reach the burner section without any problems due to low viscosity, low concentration of particles and the absence of asphaltenes. The fuel oils should not be preheated to high temperatures because more energy is required to preheat the fuel oils to a higher temperature than a lower temperature and better lubrication at lower temperatures.

In conclusion, it is recommended that unfiltered LFO be used at lower temperatures (25–60 °C) for best performance and HFO should be filtered before use at lower temperatures (25–60 °C) for best performance. Unfiltered MFO should be used at 60 °C because MFO requires to be preheated before use to avoid wax solidifying in the equipment.

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