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Case Study

Water molecules influence the lubricity of greases and fuel

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ABSTRACT

Water and lubricants interaction though not desirable but it is unavoidable. Water amplifies the corrosion at the lubricated contacts however its influence on the tribology of fuels, oils and greases is not clear, yet. Here, we have used the testing methods like Four Ball Tester (ASTM D2266, D2596) and Low Temperature Torque Tester (ASTM D1478) to investigate the effect of water on calcium sulfonate (CaS) grease, lithium (Li) grease and the test method HFRR (ASTM D6079) to study the effect of water on diesel fuel lubricity. Addition of water and an increase in its concentration in CaS and Li greases increases the roughness of friction profile and also the wear. For example, in CaS grease, the rougher friction profile indicates severe metal-to-metal contacts due to loss of boundary lubrication triggered by poor oil bleeding. This process, leading to increase in wear, is attributed to the emulsion stability that increases with an increase in water concentration, related to its interaction with $CaCo_3$ in CaS. Furthermore, such an interaction is the reason for an increase in the run-in torque with an increase in concentration of water molecules for CaS operating at – 30 °C. In the case of diesel lubricity, the water molecules interact with the polar groups in the fuel at high humidity and reduces its surface activity. As a result there is a rougher friction profile and an increase in the wear, similar to the tribological behavior of greases contaminated with water. Overall, the added water contamination hampers the lubrication by greases and fuel. Mainly, due to poor boundary lubrication that allow more metal-to-metal contacts and increase the wear. Therefore, a careful selection of the ingredients in greases and fuel is necessary to improve the behavior of bearings and diesel fuel pumps exposed to water.

1. Introduction

Water contaminates the grease and diesel fuel due to poor sealing system and humidity/moist air, respectively. The principle elements in the grease and diesel fuel influence the effect of water on the life of bearings and diesel fuel injection system. In grease, the water is absorbed or retained on the surface depending on its thickeners [1,2]. For example, calcium sulfonate thickener can absorb 8 times more water compared with the lithium complex type thickener [1]. Although it is preferred that grease absorbs water rather than its retention on the surface to improve corrosion resistance, but the absorbed water modifies the grease properties like the stiffness [1] and film thickness [3]. And it could alter the tribological behavior of the greases. However, the friction and wear behavior of the greases contaminated with water is to be investigated, yet.

In diesel fuel, the solubility of water molecules depend on the humidity and hydrophilic nature of the fuel [4]. Biodiesel with polar groups is more hydrophilic compared to diesel and it can hold 2.5 times more water molecules compared to diesel. Such a condition can weaken the surface activity of additives in the fuel and increase the wear due to poor boundary lubrication [4–6]. Water content in the fuel could also be influenced by the temperature, for example, the water content in fuel decreases with an increase in temperature [6]. Therefore, temperature and humidity are two important parameters that can affect the water contamination of diesel and its lubricity.

In this study, we have compared the wear preventive and extreme pressure resistance behaviors of two types of commercially available grease. Each type of grease was tested either with or without added water. Also, diesel with added biofuel was tested for its friction behavior in a controlled environment chamber (humidity and temperature). Industrial standard techniques like four ball test, low temperature torque test and high frequency reciprocating rigs (HFRR) were used in friction measurements. Optical microscopy was used to image and measure the wear scar. Overall, friction and wear data from the greases and diesel fuel were used to evaluate the role of water molecules in lubrication.

Abbreviations: CaS, Calcium sulfonate based grease; Li, Lithium based grease; HFRR, High frequency reciprocating rig; MWSD, Mean wear scar diameter; WP, Wear preventive; EP, Extreme pressure.

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2. Materials and methods

2.1. Greases

Calcium sulfonate grease of NLGI grade 2 (Optimax CSC-2, Optimax USA, Virginia, USA) and Lithium grease of NLGI grade 0 (Optimax 7700, Optimax USA, Virginia, USA) were used in this study. Water was added at 10%, 20% and 50% weight of grease. Later the water and grease was mixed manually until the saturation was achieved. Greases without water, that is, 0% water was used as a control. Totally there were 4 types of calcium sulfonate based grease and lithium based grease.

2.2. Diesel

Shell V-Power diesel (Shell gas station, Groningen, the Netherlands) was used in this study. The properties of the Shell V-Power diesel can be found in this reference [7]. Water contamination of the diesel was controlled by increasing the humidity and temperature in the test environment.

2.3. Friction coefficient of greases

Friction coefficient of the greases was determined using the Ducom four ball tester (TR-30PNU, Ducom Instruments Pvt. Ltd., India) and Ducom low temperature torque tester (TR-512, Ducom Instruments Pvt. Ltd., India). Friction coefficient in the four ball tester and low temperature torque tester was measured according to the test method ASTM D2266 [8] and ASTM D1478 [9], respectively. Greases were also tested for their extreme pressure or load bearing behavior using the four ball tester and according to the test method ASTM D2596 [10]. The data acquisition and analysis was through a Labview based Winducom 2010 software (Ducom Instruments Pvt. Ltd., India).

Four ball tests (ASTM D2266 and ASTM D2596) were conducted for calcium sulfonate grease (0%, 10%, 20%, 50% water in w/w) and lithium grease (0%, 10%, 20%, 50% water in w/w). And the low temperature torque test was conducted for calcium sulfonate grease with 0%, 10% and 20% water at − 30 °C. Please refer to Table 1 for more description of the testing parameters used in this study.

2.4. Friction coefficient of diesel

Friction coefficient of Shell V-Power was measured using the Ducom HFRR (Ducom Instruments Pvt. Ltd., India). And the test method was according ISO 12156-1: 2006 [11]. Friction coefficient of the diesel fuel was measured at three different humidity (35% Rh, 50%Rh, 75%Rh) and temperature (30 °C, 60 °C, 80 °C) conditions. Note that the temperature (varying humidity) and humidity (varying temperature) was fixed at 30 °C and 35%Rh, respectively. Please refer to Table 1 for more description of the testing parameters used in this study.

2.5. Wear analysis

Wear on the balls after the friction test of greases and diesel fuel were measured using an optical microscope (Olympus Vanox-T, Leica Microsystems B.V., Netherlands). Two-dimensional images of the wear track on the ball was captured using a camera built in an optical microscope. All the samples were cleaned according to the ISO 12156-1: 2006 test method before imaging the wear track. The mean wear scar diameter (MWSD) on the ball was calculated by the Eq. (1),

$$\text{MWSD} = (x + y)/2 \quad (1)$$

where x is the scar dimension perpendicular to the oscillation direction (in μm) and y is the scar dimension parallel to the oscillation direction (in μm). The scar dimension (x or y) is an average of three readings.

3. Results

Fig. 1 represents the four ball test results for calcium sulfonate grease (CaS) and lithium grease (Li). In absence of added water the CaS shows lower friction compared to Li (Fig. 1A and B). Addition of water disturbs the stable friction profiles, making it more rough and unstable for both the CaS and Li greases. In general, the friction profiles of Li grease with added water (10–50%) is rougher compared to friction profiles of CaS grease. Wear scar diameter for CaS is higher than Li grease before adding water (Fig. 1C). Addition of water increases the wear, reaching a maximum wear scar of 0.77 ± 0.056 and 0.75 ± 0.016 at 50% water, for CaS and Li grease, respectively. Load bearing capability of CaS grease is higher than Li grease, according to the extreme pressure test (Fig. 1D). Compared to Li grease the load bearing capability of CaS grease in unaffected due to the addition of water up to 20%. And at 50% water the load bearing capability of CaS drops by 1.6 times that of CaS without added water. Load bearing capability of Li grease decreases with an increase in the added water content.

Error bars represent the standard deviation over three independent measurements.

Fig. 2 represents the friction behavior of CaS with 0%, 10% and 20% water at − 30 °C. Generally, the friction is high at the beginning of the test (called as run in friction) which decreases and stabilizes until the end of the test (Fig. 2A). The run in friction increases linearly with the added water content (Fig. 2B).

Fig. 3 represents the friction and wear results for diesel fuel at different temperature and relative humidity, as obtained using the HFRR. As shown in Fig. 3A, friction profile is influenced by humidity and its profile is rougher at 75% Rh compared to 35% or 50% Rh. Temperature effect on the friction profiles is shown in Fig. 3B. Friction coefficient increases from 0.28 to 0.37, as the temperature is increased from 30 °C to 80 °C. The friction profile t at 80 °C is rougher compared to 30 °C or 60 °C. The wear scar profiles on the ball (as shown in the Fig. 3C) was used to measure the mean wear scar diameter and it was compared with the temperature and

Table 1
Testing parameters used for friction and wear characterization of lubricants.

	Ducom four ball test	Low temperature torque test	High frequency reciprocating test (HFRR)
Lubricants	CaS and Li based grease (flooded test)	CaS based grease	Shell V-Power diesel fuel
Specimens	EN52100 Steel	Ball bearing packed with grease	EN52100 Steel
Test methods	**ASTM D2266** – WP test, steady load at 40 N, 75 °C, 1200 rpm, 60 min **ASTM D2596** – EP test, steady load up to 800 N, 1770 rpm,10 s, 21 °C	**ASTM D1478** – LTT test, 4.5 N, 1 rpm, − 30 °C	**ISO 12156-1: 2006** – HFRR test, 2 N, 60 Hz, variable temperature and humidity
Contact motion	Rotating ball pressed against three fixed balls	Rotating ball bearing with radial load	Reciprocating ball on a fixed disk

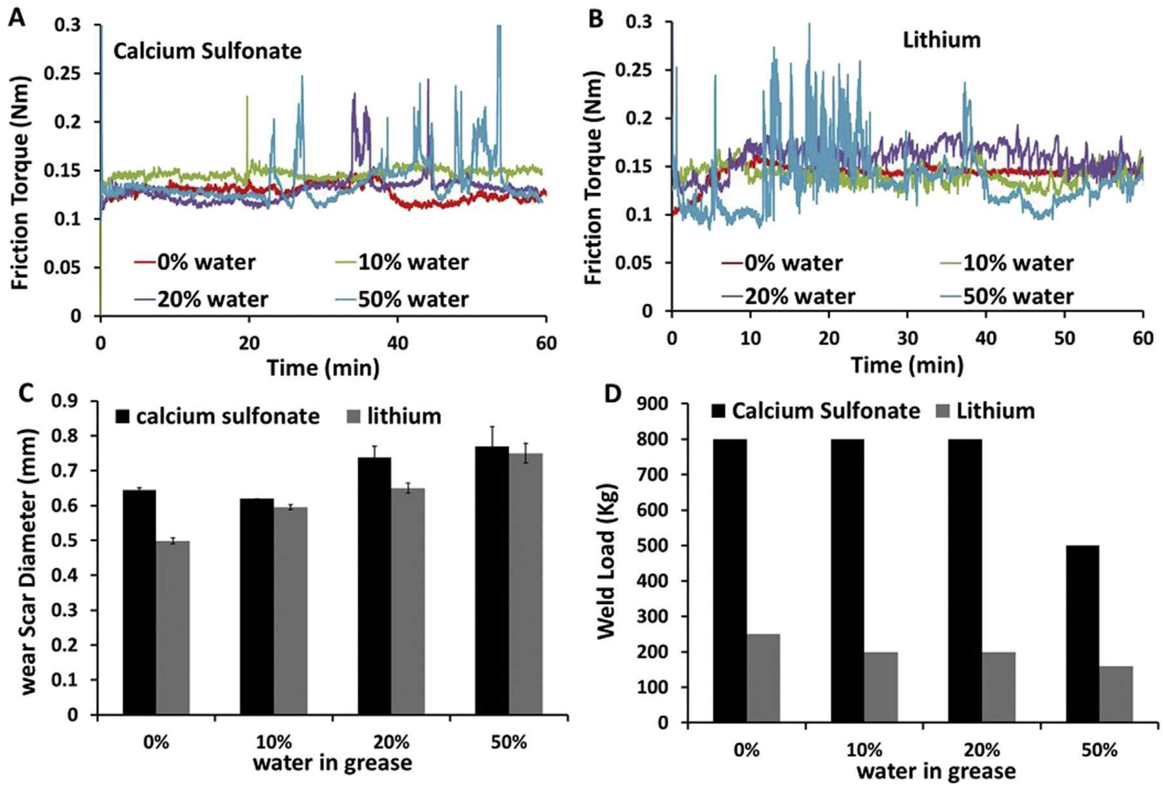

Fig. 1. Four ball test results for calcium sulfonate and lithium ion grease at 0%, 10%, 20% and 50% water. A. real time acquisition of friction profile for different calcium sulfonate greases. B. real time acquisition of friction profile for different lithium greases. C. comparison of wear scar diameter for different calcium sulfonate and lithium greases. D. weld load (or load bearing capability) numbers for different calcium sulfonate and lithium greases.

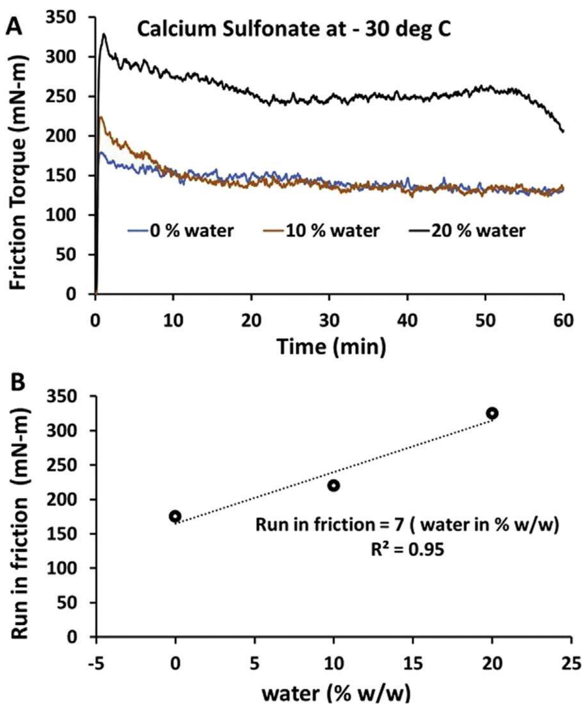

Fig. 2. Low temperature torque test for calcium sulfonate grease at – 30 °C. A real time change in friction for calcium sulfonate grease with 0%, 10% and 20% water. B. relationship between the run in friction torque and added water content (% in w/w).

humidity (Fig. 3D). Wear on the balls increased with an increase in humidity and temperature. The maximum mean wear scar diameter for Shell V-power diesel was 335 μm and 310 μm at 60 °C and 50% Rh, respectively.

4. Discussion

4.1. Water and grease interaction

Addition of water to the grease hampers its lubrication and increases the friction and wear, as determined by the four ball test and low temperature torque test. Calcium sulfonate (CaS) and lithium (Li) thickeners are polar and are the preferential source of interaction for water molecules. It was determined that increasing the water content in CaS grease will decrease its oil bleeding [1,12], EHL film thickness [3] and softness [1,2] whereas the opposite effect was observed for Li based grease [1]. Decrease in oil bleeding, for CaS grease, could be the reason for an increase in rougher friction profiles and wear, as shown in this study. We hypothesize the following mechanism for water induced changes in the CaS based grease. CaS based grease is made of $CaCo_3$ particles (natural boundary lubricant) stabilized by polar calcium sulfonate surfactants suspended in the mineral oil. Polar calcium sulfonates interact with $CaCo_3$ through anionic – cationic interaction to form micelle like structures with $CaCo_3$ at its core. Water interacts with the $CaCo_3$ to form $Ca(OH)_2$ layer and also water interacts with hydrophilic tail of the sulfonate groups that increases the emulsion stability [13]. Emulsion stability of CaS increases with the water concentration. And, it prevents the surface activity of $CaCO_3$ and also decrease an effective oil bleeding that results in an increase in metal-to-metal contact. Therefore, we observe a poor tribological behavior by CaS grease contaminated with added water. However, an increase in the oil bleeding by Li grease due to an increase in the water content [1] was not sufficient to improve the tribological behavior of Li grease.

Furthermore, it is also important to note that the load bearing capability that is defined as the load at which the welding occurs

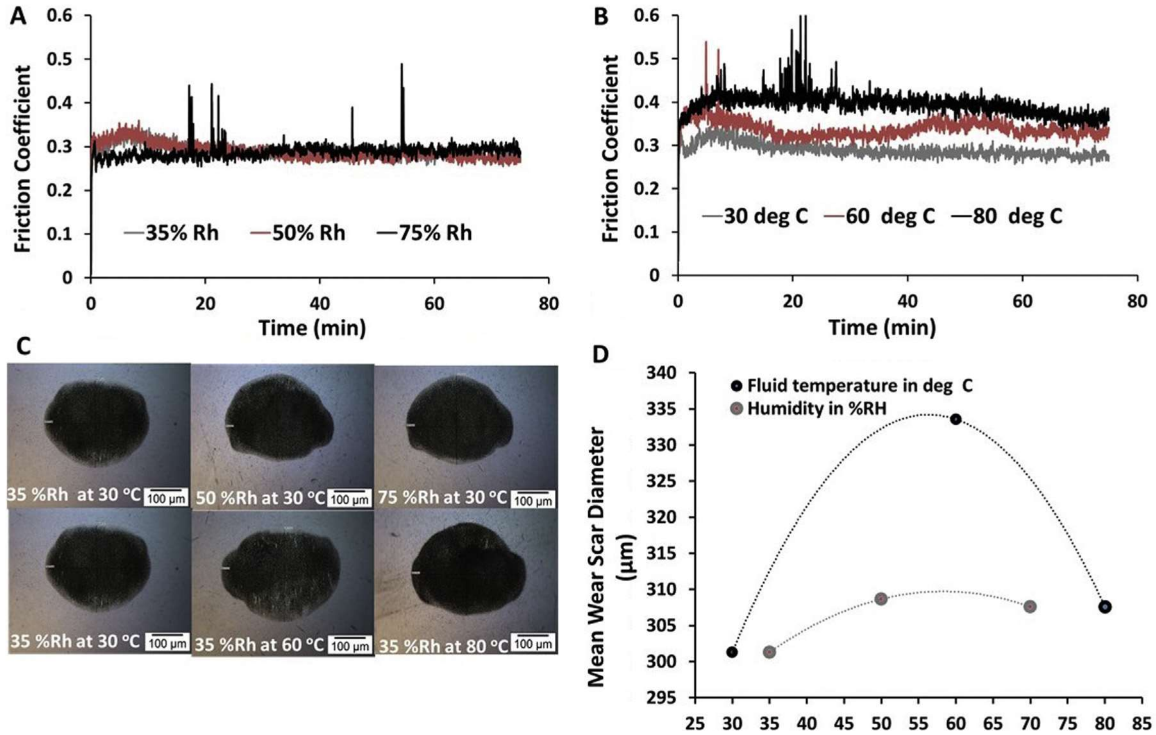

Fig. 3. HFRR lubricity test results for Shell V-Power diesel fuel. A real time acquisition of friction coefficient at 35% Rh, 50% Rh and 75% Rh. B real time acquisition of friction coefficient at 30 °C, 60 °C and 80 °C. C wear scar images of the ball at different humidity and temperature conditions. D relationship of the wear scar diameter with the temperature and humidity.

due to an increase in metal-to-metal contacts and lubricant starvation was not influenced by water concentration up to 20% for CaS grease. Unlike to the friction and wear test of CaS at 40 N (according to ASTM D2266), the load bearing test (or extreme pressure test) was conducted at a range of 160 N to 800 N (according to ASTM D2596). At high loads, atleast 4 times higher than the load used in friction and wear test, there is a sufficient oil bleeding and surface activity of $CaCo_3$ that is not influenced by added water.

Generally, the grease stiffness increases at low temperature that results in high run in friction that inflicts damage to the bearings [14]. For CaS grease, increase in the water content increases its stiffness and we show that it increases the run in friction. Furthermore, it confirms that the increase in added water to CaS will increase its emulsion stability (as explained earlier) that reduces the oil bleeding to hamper the grease lubrication during the low temperature operating condition.

5. Fuel and water interaction

The solubility of water in the fuel (or water content in the fuel) increases with the environment humidity and decreases with the sample temperature [6]. Although water adds more oxygen molecules that could increase the fuel combustion efficiency however it can interact with the polar molecules in the fuel. The polar molecules adsorb on the surface to reduce the friction and wear however its effect is minimized due to water therefore there is an increase in the wear [6]. We also observe an increase in wear with an increase in humidity however there is no increase in friction except that there is rougher friction profiles at high humidity (or high water content). However, the friction of fuel increases with the sample temperature, as shown in our results. At high temperature of 80 °C the friction profile is rougher but its wear is lower compared to 60 °C. Increase in temperature will increase the oxidation, decrease the water content and also the viscosity of the fuel. The low wear at 80 °C can be attributed to the low water content in the fuel (allowing the polar molecules to exhibit its lubrication behavior) and formation of a protective oxide layer (ferrous oxide and fuel additives). And the high friction with rougher profiles at 80 °C can be due to the breaking and reformation of the asperities during the shearing.

6. Conclusions

In this work, the friction and wear behavior of lubricants is hampered by added water. The experimental results from four ball tester, low temperature torque tester and high frequency reciprocating rig indicates the following,

1. The signature effect of water contamination is that it turns the stable friction profile into a rougher and unstable friction profile due to an increase in metal-to-metal contacts, as observed for greases and fuel.
2. Loss of tribological behavior of CaS grease (ASTM D2266) can be related with the decrease in oil bleeding and poor surface activity of $CaCo_3$ additives due to an increase in water contamination (10%, 20% and 50%).
3. Load bearing capability (ASTM D2596) of CaS grease is not influenced by water contamination up to 20% of its weight. This could be due to high operating loads where the oil bleeding is not influenced by water contamination of up to 20%.
4. At − 30 °C, for CaS grease, the run-in friction torque shows a linear increase with the concentration of added water. It confirms that the effect of water on poor oil bleeding and tribological behavior is also prevalent at −30 °C.
5. For Shell V-power diesel fuel, an increase in humidity will hamper its lubricity. This is related to an increase in the interaction between water (due to humidity) and polar groups in the

fuel that allows few polar groups to interact with the metal surface and exhibit poor boundary lubrication.

6. For Shell V-power diesel fuel, an increase in the temperature from 60 °C to 80 °C, reduces the friction and increases the wear. Lower friction can be attributed to decrease in the water content and low wear is due to formation of protective oxide layer, due to increase in temperature.

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