Bronze-Steel Friction Characteristics under the Lubrication of Modified Water/Glycerol Mixtures

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Mechanical Engineering, master's level (120 credits)
2017

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Abstract

Increasing environmental awareness has driven a lot of research to look into various environmentally friendly lubricants which can replace more conventional mineral oil based lubricants. This is true in particular for marine and hydropower applications where the risk of lubricant leakage can be damaging to the local environment. Glycerol is an organic compound produced as a byproduct when producing Biodiesel. It is environmentally friendly and has been used by the pharmaceutical and food industries for a long time. Recent research has shown that glycerol has very good tribological properties and can be used as a lubricant in some applications. However, its high viscosity and high static friction are disadvantageous and needs improvement. The purpose of this study is to investigate possible surface active environmentally adapted additives in glycerol and water solutions. 14 additives have been selected for testing and were tested in a pin-on-disc start-stop friction test to see their effect on the static and dynamic friction coefficients. From these 14 additives two were selected due to their superior performance and were further studied. The effect of concentration of water and additive in glycerol was also investigated using the same test conditions. A phosphor based additive has been found to be the best performing.
# Table of Contents

1 Introduction .......................................................................................................................... 1  
2 Literature Review ................................................................................................................ 3  
   2.1 Sliding Speed vs. Friction: Stick-Slip and Shudder Behaviour ....................................... 3  
   2.2 Glycerol as a Lubricant .................................................................................................. 4  
   2.3 Water as a Lubricant ..................................................................................................... 5  
   2.4 Role of Additives in Lubrication ...................................................................................... 6  
3 Aims and Objectives ............................................................................................................ 9  
4 Experimental Methodology ................................................................................................ 9  
   4.1 Materials ......................................................................................................................... 9  
   4.2 Tribo-Testing .................................................................................................................. 10  
   4.3 Contact Angle Measurement .......................................................................................... 13  
5 Results .................................................................................................................................. 14  
   5.1 Pure Glycerol Solutions ................................................................................................. 14  
   5.2 1% Additive in Glycerol and 10 w.t.% Distilled Water .................................................... 15  
   5.3 1% Additive in Glycerol and 20 w.t.% Distilled Water .................................................... 17  
   5.4 Effect of Additive Concentration .................................................................................... 18  
   5.5 Contact Angle ............................................................................................................... 20  
Conclusions and Future Work ............................................................................................... 21  
References ............................................................................................................................... 23
List of Figures

Figure 2: Shows the structure of a friction modifier and how it operates in contact ...................... 8
Figure 4: Variation of RPM vs time for the Tribo-test .................................................................. 11
Figure 5: Shows the coefficient of friction plotted vs. sliding speed for glycerol and how $u_1$ and $u_{50}$ are chosen .................................................................................................................. 12
Figure 6: STFi Contact Angle Measurement Device .................................................................... 13
Figure 7: Shows the static to dynamic friction ratio for glycerol and its water solutions .......... 14
Figure 8: Shows the static and dynamic friction coefficients for glycerol and its solutions ...... 15
Figure 9: Shows the static to dynamic friction ratio for the additive solutions .......................... 16
Figure 10: Shows the static and dynamic friction coefficients for the additive solutions ........ 16
Figure 11: Comparing the static to dynamic friction ratio of additives solutions in 10w.t.% and 20w.t.% ........................................................................................................................................ 17
Figure 12: Comparing the static and dynamic friction coefficients of additives solutions in 10w.t.% and 20w.t.% ........................................................................................................................................ 17
Figure 13: Shows the effect of Ionic Liquid concentration on static to dynamic friction ratio .... 18
Figure 14: Shows the effect of Ionic Liquid concentration on static and dynamic friction coefficients ........................................................................................................................................ 18
Figure 15: Shows the effect of No. 1 Phosphor Based concentration on static to dynamic friction ratio ........................................................................................................................................ 19
Figure 16: Shows the effect of No. 1 Phosphor Based concentration on static and dynamic friction coefficients ........................................................................................................................................ 19
Figure 17: Static friction coefficient vs contact angle for several additive and pure glycerol solutions on the Bronze Surface ........................................................................................................ 20
Figure 18: Static friction coefficient vs contact angle for several additive and pure glycerol solutions on the Steel Surface ........................................................................................................ 20
1 Introduction

Self-lubricating bearing materials are materials that are able to slide against a metal counter surface; typically steel, at the required load and speed in dry conditions without suffering the damages that would normally occur in such conditions [1]. They have been widely adapted and used instead of conventional grease and oil in many different applications; such as hydropower and marine applications. The use of self-lubricated materials is becoming essential because of the damages that may occur from lubricant leakage in the environment. Other applications, particularly aerospace applications, cannot use lubricants in their bearings due to the lack of vapor pressure or extremely low/high temperatures which eliminates the possibility of lubrication.

There is a wide variety of self-lubricated bearings that differ in operating principles; some are made by using solid lubricants and applying them as a film on a metallic surface, or they are made as composites with solid bindings embedded in the surface structure [2]. Self-lubricated materials are required to perform their function without performance degradation, sometimes up to 20 years, due to difficult maintenance setups or sensitive operation conditions. This is not an easy task, particularly since predicting bearing performance under these conditions is difficult due to the number of parameters needed to be considered, such as; material properties, wear particles, wear rate and surface roughness. In hydropower applications, where the sliding speeds might be very low and the loads extremely high, improving friction and wear resistance is of paramount importance. Therefore, the use of some lubrication in these contacts is presenting itself as a solution to that problem again; it becomes necessary.

However, simply lubricating the contact with conventional lubricants, especially in marine and hydropower applications, is not the proper solution. With the increasing environmental awareness, the negative impact of lubricants based on mineral oils has been realized. Mineral based oils are harmful and toxic to aquatic life, can bioaccumulate, are not readily biodegradable and can contaminate ground waters for extended periods of time and inhibit plant growth. This is very problematic since it has been estimated that about 10 million tons of mineral based oil and hydraulic fluids are leaked into the environment in an uncontrolled manner leading to contamination [3]. This is also particularly problematic for engineering applications where the equipment is meant to operate in hydropower plants, agricultural applications, food and medicine production. In these applications, the leaked lubricants potentially contaminate fresh water drinking supplies, agricultural land or food sources for humans.

Mineral or synthetic oils and their additives contain harmful substances such as; cyclic aromatic hydrocarbons, lead, cadmium, zinc, phosphorus and chlorine that have well documented harmful effects on the environment [4]. The search for green lubricants is driven by the desire to steer away from such chemicals due to the risk of leakage. In recent research [5], water, vegetable oils and glycerol have been studied as viable alternatives for currently used lubricants in multiple applications. Although vegetables oils have shown progress in replacing mineral oils in food packaging and pharmaceutical applications, their low oxidative stability, narrow viscosity range and flow characteristics at low temperatures inhibit them from being used widely.
Water is one of the oldest lubricants known to man. Some of the advantages of using water as a lubricant is that it is inexpensive, abundant, non-flammable, relatively incompressible and has low viscosity. However, it also has high corrosive properties, low freezing and boiling points, and poor lubrication and load carrying properties. This can be overcome by adding additives [4], but most of these additives are toxic and harmful to the environment as well, and are also sometimes insoluble in water. To solve this problem, a particular type of environmentally adaptable lubricants (EALs) can be formulated from mainly either water-based or glycerol-based lubricants with environmentally friendly additives to improve their lubrication, corrosion and wear resistance properties.

In recent times, the increasing environmental awareness has been driving the production of bio-diesel from various biological products such as vegetable oils. This is done by conventional transesterification of triglycerides which inevitably produces glycerol as a byproduct. On average for every 10kg of bio-diesel produced, 1 kg of glycerol is formed as a byproduct [6]. Glycerol is mainly used in pharmaceutical applications, food production, personal care and various other industrial processes. It is environmentally friendly and non-toxic. However, there is a surplus of glycerol mainly driven by the increase of bio-diesel production and the limited number of applications for the glycerol to be used in. Recently, various research studies have discovered that glycerol can produce very low coefficients of friction in boundary and elasto-hydrodynamic regimes [7]. In DLC coated contacts, the friction coefficient was hardly measurable and can almost be described as super-lubrication. The reason was attributed to the sp2-carbon atoms in the coating which reacted with the glycerol leading to its degradation and the formation of an easily shearable water layer.

This is an indication that glycerol could have various lubrication applications. Moreover, since it is environmentally friendly and available as a byproduct of existing industrial applications, glycerol could be used to reduce friction and wear in self-lubricated bearings operating in applications where environmental leakage is unacceptable. However, most studies on glycerol have been performed for full-film or mixed operating conditions and boundary lubricating conditions have been largely neglected. In boundary lubrication, the friction characteristics with sliding speed is especially important, since it affects the risk of machine vibrations due to stick-slip. There is very limited information about the friction behavior of glycerol and glycerol aqueous solutions available in literature.
2 Literature Review

The study of the behavior of glycerol and glycerol aqueous solutions in Boundary lubrication under low sliding speeds has not been covered in literature either. The reasons as to why this behavior is important are discussed in this chapter.

2.1 Sliding Speed vs. Friction: Stick-Slip and Shudder Behaviour

Stick-slip and shudder behaviour are well known problems in lubricated contacts which engineers try to avoid in different applications such as clutches. Stick-slip usually occurs when the transition from static to dynamic friction is discontinuous while shudder is self-induced vibration due to the negative slope of the friction versus sliding speed [8] as shown in Figure 1. In general this behavior is undesirable because it leads to machine failure and increased wear, particularly in machinery where the mode of operation requires frequent start-stop cycles, and operates under low sliding speeds. Knowledge gained from studying the process of designing a clutch to avoid these phenomena can help understand the improvements required for producing glycerol-based aqueous solutions.

Both of these phenomena can be avoided by having a positive slope in the $\mu$-v curve. A ratio developed by Ohtani et al [9], called the $u1/u50$ defined as the ratio of the coefficient of friction at 1 RPM end at 50 rpm which is desire to be below 1 in order to completely avoid stick-slip and shudder behavior. However this ratio is not enough to completely predict whether a system would avoid undesirable behavior or not. It can be assumed that any region in the friction versus speed curve that displays a negative slope will lead to either one of these behaviors. Although for typical operation, the coefficient of friction generally decreases with increasing sliding speed, if the transition is not smooth enough stick slip or shudder might occur. In wet clutches a positive slope is desired which is usually achieved by careful design of lubricant chemistry and friction material. There are several explanations to how this is possible however the exact reason is not confirmed [10]. It can be however be linked to a unique interaction between the friction material and the friction modifiers in the lubricant.

Several studies, including preliminary tests in this study, have shown that glycerol has a negative slope; as shown in Figure 1, when plotting the coefficient of friction versus the sliding speed. The exact reason for glycerol’s high static friction is not known. Several hypotheses have been formulated from observations during the experimentation period. The main reason is believed to be related to the wetting properties of the lubricant in relation to the surface. It is thought that meniscus forces formed on the Nano-level where the lubricant can be trapped between asperities can lead to increasing friction during shearing. Gonzales et al. [11] showed that lower contact angles can be correlated to higher load carrying capacity and a slight increase in friction coefficient. It is believed that the relatively low contact angle of a lubricant aids in the formation of lubricant films that can reduce wear but are harder to shear. Although the study was not conducted on glycerol, further experimentation could shed light on whether this is the reason or not.
2.2 Glycerol as a Lubricant

Glycerol (C₃H₈O₃) is a fluid that is odorless, colorless and very viscous. Pure glycerol has a freezing point of 18°C [11] and a viscosity of 890 Pa.s. at room temperature [12]; which is much higher than most mineral-based oils. The efficiency of a lubricant mainly depends on its viscosity, the structure and the additives at the surface composition. When the lubricant has high viscosity, it forms a thick tribo-film which decreases the friction and the wear; because the layer separates the contacting bodies [5].

It was found that, in general, pure glycerol as a lubricant produces low friction coefficients, and has higher wear resistance and lubricant stability than synthetic base oil lubricants. Also, glycerol-based lubricants in plug valves prevented the metals from corrosion, and were therefore also used in internal combustion engines. However, when the tribo-film fails, the mechanism of the lubrication becomes very complex.

Studies show [5,13] that the low freezing point and high viscosity of glycerol is actually unwanted because more energy is required to shear it and so the temperature of the system increases; which in turn increases the decomposition of the lubricant and leads to the failure of the materials surface. However, the freezing point and viscosity of pure glycerol can be decreased by adding water. When mixed with water, the freezing point of glycerol can be lowered to -50 °C, and the viscosity can become 100 times lower in a 50% w/w mixture.

In the study done by Shi et al.(2014) [5], the boundary and elastohydrodynamic lubricating regimes of glycerol and glycerol-water mixtures were investigated in rolling and sliding contacts using a ball-on-disc setup that allows for variation in the rolling speed of the ball; hence,
allowing for testing under different slide-to-roll ratios (SRR). The test was also conducted on rapeseed base-oil for comparison with a synthetic base-oil.

In their study, the friction coefficient for rapeseed oil and glycerol water mixtures below 20% showed an increasing trend, implying that full film lubrication is achieved. For higher concentrations of water, however, the friction coefficient was higher even at low SRR, and in some cases even had a decreasing friction trend. This was claimed to be due to the lower viscosity of the mixture and the inability to form a fluid film to separate the surfaces. After a running-in period of about 15 mints, the friction coefficients of the glycerol-water mixtures upto 20 wt% reached a steady state. After the running-in period, the friction coefficients decreases for the mixtures with higher water content.

It was also shown that a glycerol-water mixture of 50% w/w had a 100 times lower viscosity compared to pure glycerol, yet the wear rate was 12 times higher. The severe wear in the glycerol water mixture is evident through a pile-up on the wear track edges, and fatigue failure due to spalling was also evident. Although glycerol-water mixture has a lower viscosity than pure glycerol, the failure modes can be considered catastrophic. Water in glycerol is also corrosive and promotes wear in steel.

The results also showed that the film thickness of aqueous glycerol solutions are linear to the entrainment speed up to 30% by weight of water, and full film elastohydrodynamic lubrication can be achieved. With higher water content, the fluid film collapses and the contact moves into mixed or boundary lubrication depending on percentage of water content. Thus, glycerol aqueous solutions show great promise to be used as a green lubricant and as a replacement for conventionally used lubricants; when the proper water content percentage is used.

Another study done by Tortora et al. in 2017 [13], investigated the stability of the glycerol-water mixture lubricants. They used the same concentrations as the previous study and they also confirmed that the friction and wear increase with increasing water content, causing fatigue failure of the lubricated disk. In this study the mixtures were compared to motor oils 5W30 and 5W40. In their study they have found that pure glycerol exhibited stable lubrication properties making it suitable for use as a replacement for mineral base oil.

2.3 Water as a Lubricant

Water is one of the oldest lubricants in history, and has been used since the ancient Egyptian times; for the transportation of statues [14]. Although water -based/ aqueous lubricants have gained a large interest of the years because of their nature; being non-toxic, biodegradable, environmentally friendly, abundant, fire resistant, etc, they still have major disadvantages as a lubricant; mainly being non-viscous and highly corrosive [15]. In the last few decades, extensive studies have been made on using aqueous solutions as lubricants; also for the intention of it replacing petroleum in many applications. However, big challenges still occur in the understanding of the characteristics and mechanisms of aqueous lubricants due to the diversity and complexity of aqueous solutions [16].
Water lubrication is a complicated physical process, and cannot be understood without understanding the friction and adhesion characteristics of water molecules on the nano-scale [17, 18]. Therefore, using recently developed nanotechnological processes, water lubrication was studied using AFM, SFA, X-ray diffraction and optical interferometry. The confinement of water molecules in small places in the contact prevents the formation of directional hydrogen bonds; these bonds are not easily shearable and may lead in an increase friction. In low confinement, 0.2±0.2 nm, the viscosity of a water film with low ion presence was reported to range from $10^3$ to $10^7$ Pa.s compared to $10^{-4}$ Pa.s normally. For the same separation and with higher ion concentrations the water was bounded to the surfaces and remained very fluid during shearing, creating what was called as hydration layers. This hydrated layer can perform as an efficient lubricant and can support high normal loads.

The rise in viscosity, however, for pure deionized water is not nearly as comparable. By using a setup which combines optical interference with a ball-on-disc setup, the minimum film thickness of a water lubricant can be measured [15]. It has been proven that pure water has a poor film formation capability due to its low viscosity. It was predicted using the Hamrock-Dowson EHL theory, that in elastohydrodynamic regime, at a sliding speed of 5m/s the film thickness was less than 10nm [19]. The lubrication qualities of water however, can be improved by using additive solutions; which will be explained in the next section.

Ratio and Spikes in 1999, experimented on the film forming abilities of several types of surfactant aqueous solutions using an interferometer rig similar to the one described previously. The surfactant has a unique amphilic structure, which can migrate to the water surface and alter its properties, therefore influencing the lubricating properties. In this case, the film formation showed a dependence on surfactant type and concentration. By creating mono or bi-layers through adsorption, the solution could form a film at low speeds; an effect further enhanced by hydrodynamic entrainment at higher speeds [15]. In other studies, aqueous solutions lubrication has been enhanced by using polymers such as (PTFE). They are considered as good candidates to enhance water solutions because of their self-lubricating capabilities. In the past, several polymers such as; bakelite or vinyl fluoride have been used as solid lubricants in machinery for reducing wear, friction and energy consumption. As an aqueous solution, they have been capable of improving the formation of fluid films and can even forming protective films in boundary regimes causing low friction coefficient [20].

### 2.4 Role of Additives in Lubrication

As mentioned earlier, there has been an increasing interest in replacing mineral and synthetic oils with non-toxic base oils to protect the environment. Most additives that are used to obtain the required mechanical and tribological properties in these base oils, also contain compounds that are very harmful to the environment; such as, phosphorous, lead, zinc, chlorine and cadmium [4]. Hence, there has been in increase in interest in replacing them with environmentally friendly additives as well. When aqueous solutions are used as a base lubricant, additives are needed to
manage their lubricating and corrosive properties. However, these additives should also satisfy the ecological criteria set for the environment; standard additives would be toxic and insoluble.

Friction modifiers are lubricant additives that are designed to lower the surface friction of liquid lubricated parts in sliding and rolling contacts; boundary and mixed lubrication regimes. They are widely used in engines and many other applications, because they reduce engine wear and noise, prevent micropitting of metal surfaces when used in industrial gear lubricants, and they can also prevent metal scoring [21]. Friction modifiers are made of polar molecules that have a polar head and an oil-soluble tail, where the polar end attaches to the metal surfaces and the oil-soluble tail acting upwards; as fibers standing up as shown in Figure 2. These molecules then act like cushions or coatings reducing friction. There are four classes of friction modifiers; the first are organic friction modifiers, also known as amphiphilic surfactants, such as free fatty acids derived from fats and vegetable oils. The second class are the oil-soluble organo-molybdenum compounds such as the well known MoDTC friction modifier (molybdenum dithiocarbamate) that form low shear strength. The third are functionalised polymers which are known as viscosity modifiers that reduce friction in the hydrodynamic regime. The fourth class includes friction modifier additives that are made of dispersed nanoparticles; which have many types and shapes [21]. The main problem facing this study is that; compared to mineral oils, not a lot of work has been done on friction modifiers that can operate in a polar solution.

The alkyl polyglucosides (APGs) are one group of those additives. These are surfactants that are environmentally friendly and also do not require any utilization because they are soluble in water [4]. Proper concentrations and appropriate temperatures and pressures allows APG to produce micelles which can organize themselves to form lyotropic Liquid Crystals. Therefore the spatial arrangement allows them to affect the tribological properties similar to when graphite and molybdenum disulfide are used as additives. Alkyl polyglucosides are produced commercially making them relatively cheap since they are synthesized from palm oil or coconut.

In the study done by Sulek and Wasilewski 2006 [4], two forms of APGs; C8-C10 and C12-C14, were tested using the four-ball tester and the ring-on-disc contact tester to investigate their tribological properties. The molecular structure of APGs affect their solubility in different solvents. Those containing between 6 and 14 carbon atoms are water soluble, however those containing between 16 and 22 carbon atoms are oil soluble. The degree of polymerization affects the solubility in polar mediums, while longer alkyl chains lead to a solubility in nonpolar mediums. The four ball tester used chrome bearing steel balls, and the results showed that the friction coefficient of pure water start at 0.2 and increase to stabilize at 0.5 after a running-in period. While both aqueous solutions with 1% water concentration also start at 0.2 but then decrease rapidly after some time and stabilize at a very low friction coefficient. However, the short chain APG takes more time to decrease and stabilize.

Different percentages ranging from 0.001%-50% of APG concentrations were also tested. The results showed that the friction coefficient and the wear scar diameters of the balls were highly dependent on the APG concentration. The friction coefficient seemed to drop greatly after 0.1% for both APGs, however, any increase in concentration after that had a minimal effect. The same
results were observed in the wear test and therefore it can be concluded that that the longer chains APGs (C12-C14) perform better then the shorter chains (C8-C10).

To compare both APGs at 1% concentration, the ring-on-disc contact test also using chrome bearing steel, was conducted to test the lubricants in a developed contact. Here the longer chain molecules exhibited an instability of friction coefficient compared to the shorter chain molecules. This was explained to be due to the additives having characteristic features of smoothening the surfaces where the surface roughness was reduced several times.

Other additives that have been investigated to modify the lubricating properties of aqueous solutions are sodium lauryl sulfate (SLS) and ethoxylated sodium lauryl sulfate (ESLS). They were investigated in the study by Sulek and Wasilewski 2010 [22], where both solutions were also tested using a four ball machine at a constant load 2KN using steel balls. They showed that SLS and ESLS additives both significantly improved the tribological properties of water. They contain sulfate group ($SO_4^{2-}$) which makes them soluble in polar solvents; the alkyl chain showed affinity for nonpolar solvents. The absorption of the additives on solid surfaces had a significant effect on the lubricant performance. The results showed that the alkyl sulfate solutions produced a much lower friction coefficient and had very good stability after a small running-in period. They also showed a dependency of friction coefficient and wear scar diameter of the balls on the water concentration of the alkyl sulfate solutions. The additives at 1% concentration reduced the friction coefficient value by six times compared to pure water while the wear scar diameter was two times smaller. When the water concentration was below 0.1%, the friction coefficient of ESLS was 4 times higher than that of the SLS. With increasing water concentration, the friction decreased and then increased again until it stabilized and reached a stable state. Thus it was concluded that SLS is favorable up until a specific concentration level, however it increases after that. These changes and differences are attributed to the degree of absorption of the additives at the surface, which depends on the physicochemical properties of the solutions.

Figure 2: Shows the structure of a friction modifier and how it operates in contact
3 Aims and Objectives

The aim of this project is to determine the most appropriate additives to improve the friction characteristics with sliding speed in bronze/steel systems lubricated by glycerol. These additives should be environmentally friendly and improve friction under high loads and low sliding speeds.

4 Experimental Methodology

The objectives are to investigate 14 additives in a glycerol aqueous solution of 10% water concentration, for a bronze-steel contact, to determine how different sliding speeds, under high contact loads, would affect their frictional characteristics and performance. This will be done using the experimental pin-on-disc test. The additives that will be studied belong to the following groups: Phosphor based, Amine based, COOH based, Sulfonated, PEG based, Sugar based, Ionic liquids based.

4.1 Materials

The additives investigated in this study were procured by Assoc. Prof. Yijun Shi at the department of Machine Elements in LTU. He also conducted the preparation of the samples. The additives were used as bought from the supplier.

In the sample preparation, each additive was first mixed with water, based on the appropriate w.t.%, and then the appropriate amount of glycerol was added to achieve the required w.t.%. The exact chemical composition for the additive cannot be disclosed due to proprietary reasons, but they will be referred to using their main functional group. In total, 14 additives were investigated:

1. No.1 Phosphor based
2. No.2 Phosphor based
3. No.3 Castor oil based
4. No.4 Polysulfonate based
5. No.5 Sulfonate based
6. No.6 Sulfate based
7. Polyether based
8. No.8 COOH based
9. No.9 COOH based
10. No.10 Ammonium based
11. No.11 Non-Ionic based
12. No.12 Oxide Amine based
13. No.13 Non-Ionic based
14. No.14 Ionic Liquid based
The prepared samples can be classified into 4 groups of investigation:

1. Pure solutions; where glycerol is mixed with distilled water with different w.t.%; 0%, 10%, 20%, 30%, 40% and 50%.
2. Adding 1% of additive in a mixture of glycerol and 10 w.t.% distilled water.
3. Adding 1% of additive in a mixture of glycerol and 20 w.t.% distilled water.
4. Adding 0.2%, 1% and 0.4% of additive in a mixture of glycerol and 20w.t.% distilled water.

4.2 Tribo-Testing

The Tribological tests were performed using the unidirectional pin-on-disc tribometer (TE67 Pin-on-Disc Tribometer, Phoenix Tribology, United Kingdom); shown and labeled in Figure 3. The set up used was a stationary bronze (Cu= rest , Sn= 7.5-8.5%, P=0.01-0.035%) cylindrical pin (radius=3mm, thickness=1.5mm) with a roughness of Ra=0.26μm and hardness of 180-210HB, and a rotating standard friction steel material disc with a roughness of Ra 0.34 μm. All experiments were conducted in laboratory standard temperature and pressure, using a dead weight of 8kg (78.48N) resulting in a contact pressure of 11MPa on the pin. The disc rotates in a stationary oil bath which requires approximately 120mL of lubricant for the disc to be fully submerged.

Figure 3: Pin-on-Disc Tribometer
Since the focus of this study is on the stick-slip and shudder behavior of the system, each tribo-
test conducted is 34 minutes long and is split into two parts. The first part is a run-in period 15
minutes long, where the sliding speed is kept at 0.1m/s @ 50rpm and a 17.9 mm sliding radius.
The second part of the tribo-test consists of 9 start-stop cycles, each of which consists of
bringing the rpm to 0 then accelerating to 50 rpm over a period of 1 minute with a constant
acceleration. The variation of RPM vs time is shown in Figure 4. The operating conditions were
selected to minimize the hydrodynamic effect of the material and attempt to create
boundary/mixed lubrication regimes.

![Figure 4: Variation of RPM vs time for the Tribo-test](image)

The test parameters were chosen based on a rigorous trial and error process to achieve the most
stable performance. The data received from the machine consisted of a TSV file with the time,
the rpm of the disc and the measured friction force. The data from the test was then analyzed by
splitting it into different steps; ie: run-in segments, 9 increasing and 9 decreasing speed
segments. The run-in segment data is not important for the analysis because we are interested in
change from the static to dynamic friction behavior. It was included in the test to ensure the
results are not influenced by run-in behavior. For the rest of the data, the coefficient of friction is
plotted vs. the sliding speed as shown in Figure 5. The value \( \mu_{1} \) is taken as the average
coefficient of friction at 0 - 0.01m/s sliding speed. Similarly, \( \mu_{50} \) is taken as the average
coefficient of friction at 0.09 - 0.1 m/s. All tests were repeated at least 2 times to ensure
repeatability. Table 1 shows a summary of the test conditions.
Figure 5: Shows the coefficient of friction plotted vs. sliding speed for glycerol and how $\mu_1$ and $\mu_{50}$ are chosen.

Table 1: Test Rig Conditions

<table>
<thead>
<tr>
<th>Motion and Configuration</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Pin Material</td>
<td>Bronze, 3mm</td>
</tr>
<tr>
<td>Counter Material</td>
<td>Steel</td>
</tr>
<tr>
<td>Max. Contact Stress</td>
<td>11 MPa</td>
</tr>
<tr>
<td>Applied Load</td>
<td>8 Kg</td>
</tr>
<tr>
<td>Sliding Speed</td>
<td>0-50 rpm</td>
</tr>
<tr>
<td>Cycle Time</td>
<td>2 minutes * 9 cycles</td>
</tr>
<tr>
<td>Running-In</td>
<td>15 minutes</td>
</tr>
<tr>
<td>$\mu_1$</td>
<td>0.01 m/s</td>
</tr>
<tr>
<td>$\mu_{50}$</td>
<td>0.1 m/s</td>
</tr>
</tbody>
</table>
4.3 Contact Angle Measurement

The measurement of contact angle in this study was done to see if a correlation exists between the contact angle and coefficient of friction. There is no denial that the surface wettability and the chemistry between the lubricant and the surface affects the performance. There are two prevailing theories on this effect. On one of the studies conducted by [23], it was noticed that in cases of pure water lubrication, hydrophobicity between the surface and the water lead to an improved load carrying capacity. Since the surface is hydrophobic, the water cannot spread freely and is therefore forced to coalesce and form better film lubrication. In different studies, involving additives, it was noticed that with lower contact angles and more spreading, the lubricant performed better [24, 25] This is believed to be because of better spreading, compounds such as friction modifiers have the ability to form a continuous monolayer that can improve the performance. So in this sense, the latter theory seems to apply better to our study and this test was conducted to see if there is a particular relation.

The contact angle measurement between the various glycerol solutions; pure, water and with additives, and the bronze and disc material has been measured using a STFi contact angle measurement device; shown in Figure 6. The method used was a static sessile drop (Attension Theta, Biolin Scientific products, Sweden). In this method, 4 µl of the solution was placed on one of the metal surfaces using a micro-syringe in front of a high-speed digital camera. The drop image and contact angle were recorded one second after deposition. To determine the wettability, the measurement was conducted 5 times and the average value was calculated.

![Figure 6: STFi Contact Angle Measurement Device](image-url)
5 Results

5.1 Pure Glycerol Solutions

This test was conducted in order to see how glycerol and water mixtures perform without any additives in these conditions and how the ratio $\mu_1/\mu_{50}$; described in section 4.2, changes with changing water content. The tribo-test; described in section 4.2, was performed on glycerol and distilled water mixtures with different water contents; 0 w.t.%, 10 w.t.%, 20 w.t.%, 30 w.t.%, 40 w.t.%, 50 w.t.%. Distilled water was also tested to see how much the water influences the behavior of glycerol.

Figure 7 is a bar chart comparing the $\mu_1/\mu_{50}$ ratios for the above-mentioned conditions with standard deviations. Figure 8 shows each of $\mu_1$ & $\mu_{50}$ values with standard deviation for the same conditions. It is important to consider both results carefully; since a lower ratio alone does not necessarily mean that the lubricant can perform better. A lower ratio can mean a large increase in the dynamic friction behavior.

It can be clearly seen from the $\mu_1/\mu_{50}$ graph in Figure 7 that the glycerol has the highest ratio while distilled water has the lowest. The addition of water lowered the ratio significantly for all of solutions except for the 10w.t.% which seems to have only slightly decreased compared to pure glycerol. The remainder of the water solutions seem to be operating within the same range.

![Graph showing $\mu_1/\mu_{50}$ ratios for glycerol and water solutions](image)

Figure 7: Shows the static to dynamic friction ratio for glycerol and its water solutions

From Figure 7 only, one can assume that 20%, 40%, 50% glycerol water solutions and distilled water perform better. However, further examination of Figure 8 shows that increasing the water content seems to be increasing the dynamic friction coefficient drastically. As can be seen, the dynamic friction coefficient for pure glycerol is approximately 0.05 at 0.1m/s; however, the value for water is almost 10 times as much for the same sliding speed. Further examination, shows that all glycerol solutions have
either equal or much higher static friction compared to pure glycerol; even though they have lower $\mu_1/\mu_{50}$ ratios. Since, however, the additives require water to easily disperse, the rest of this study will be concerned with 10 w.t.% and 20 w.t.% glycerol solutions only. What is very interesting about these 2 selections is that they both have roughly the same static friction which is lower than pure glycerol. However, the dynamic friction for the 10w.t.% water is lower than for pure glycerol which is why the ratio for 10w.t.% is very high.

![Figure 8: Shows the static and dynamic friction coefficients for glycerol and its solutions.](image)

### 5.2 1% Additive in Glycerol and 10 w.t.% Distilled Water

The next step of this study is to see the effect of the additives shown in section 4.1 on glycerol solutions under the same conditions. In order to do that, all additives were prepared in a 10 w.t.% water glycerol solution with 1 w.t.% additive. After that they were all tested under the same conditions described in section 4.2. Figure 9 shows the comparison of the $\mu_1/\mu_{50}$ ratio for the additives. Figure 10 shows the $\mu_1$ & $\mu_{50}$ ratios for each of the additives.

Figure 9 clearly shows which of the additives have a greater effect on the $\mu_1/\mu_{50}$ ratio. No. 14 ionic liquid seems to be having the greatest effect since it turned the slope into a positive slope. This is the desired performance from the additive since the system is expected to have a lower tendency to shudder. Another possible additive is No.1 phosphor based which has a ratio of approximately 1.2, which means it has a very positive effect on the ratio.
Further examination of Figure 10, shows how the additives improve the performance. The results clearly show how that additives No.1 and No.14 greatly reduce the static coefficient of friction. They both lowered it to below 0.05 compared to 0.25 for pure glycerol. No. 14 ionic liquid however increased the dynamic coefficient of friction slightly; suggesting that a negative interference may be occurring between the glycerol and ionic liquid lubricating mechanisms. However, the exact reason is not known. Despite that, the positive slope is a very desirable property and therefore it is actually the current best performing additive.
5.3 1% Additive in Glycerol and 20 w.t.% Distilled Water

The purpose of this test is to compare the performance of additives in solutions of 10w.t.% and 20w.t.%. From the results in section 5.1 glycerol solutions of 20w.t.% performed similar to 10w.t.% solutions. In this test the No.1 Phosphor based additive and No.14 Ionic Liquid additive will be prepared in 20w.t.% water glycerol solutions and be used to conduct the tribo-test.

Figure 11 shows the $\mu_1/\mu_50$ ratio for the additives in both 10w.t.% and 20w.t.%; while Figure 12 shows the $\mu_1$ & $\mu_50$ for the same solutions. The most interesting observation is that the 20w.t.% solutions performed slightly better on average but have a higher standard deviation. Moreover, No. 14 Ionic Liquid shows to be even have a higher positive slope in the 20w.t.% solution.

Figure 11: Comparing the static to dynamic friction ratio of additives solutions in 10w.t.% and 20w.t.%

Figure 12: Comparing the static and dynamic friction coefficients of additives solutions in 10w.t.% and 20w.t.%
5.4 Effect of Additive Concentration

The previous section of this study was focused on finding the most suitable additives for glycerol in these particular conditions. After selecting the additives; No.1 and No.14, another test was conducted to see the effect of concentration on the lubricant performance. Figure 13 shows the $\mu_1/\mu_{50}$ ratio for the ionic liquid; while Figure 14 shows the $\mu_1$ & $\mu_{50}$ for ionic liquid in concentrations of 0.2%, 0.6%, 1%, 2% and 4%. The most notable thing seen is that the additive becomes most effective after 0.6% concentration and the performance does not seem to be affected by further increasing the concentration.

![Figure 13: Shows the effect of Ionic Liquid concentration on static to dynamic friction ratio](image)

![Figure 14: Shows the effect of Ionic Liquid concentration on static and dynamic friction coefficients](image)
Figure 15 shows the $\mu_1/\mu_{50}$ ratio for the phosphor based; while Figure 16 shows the $\mu_1$ & $\mu_{50}$ for phosphor based in concentrations of 0.6%, 1%, 2% and 4%. It can be seen that in 0.6% concentration, the phosphor based additive performs better by turning the slope from negative to positive. Perhaps, further testing with lower concentrations may present further interesting observations.

![Figure 15: Shows the effect of No. 1 Phosphor Based concentration on static to dynamic friction ratio](image1)

![Figure 16: Shows the effect of No. 1 Phosphor Based concentration on static and dynamic friction coefficients](image2)
5.5 Contact Angle

As per section 4.3 the contact angle measurement was conducted in order to inspect one of the reasons why each of the additives work. Figure 17 and Figure 18 show the contact angle vs $\mu_1$ for some additives and for glycerol water solutions for both Bronze and Steel respectively. The measurement could not be conducted for all of the desired additives. This is particularly due to the high active surface nature of additives preventing control over the drop volume and result in an inability to conduct the test.

Figure 17: Static friction coefficient vs contact angle for several additive and pure glycerol solutions on the Bronze Surface

Figure 18: Static friction coefficient vs contact angle for several additive and pure glycerol solutions on the Steel Surface
The most interesting outcome is that there seems to be some correlation between the contact angle and the friction coefficient for the additive solutions and the pure glycerol solution as marked in the blue circle in both Figure 17 and Figure 18. There is an outlier for the No. 2 phosphor based additive. A similar relationship can be seen with water glycerol solutions marked by the green circle. This is not conclusive evidence but may be interesting data supporting the theory; that surface-active components perform better when the surface they are used on allows to spread evenly and cover the surface. However, further studies are required to confirm that.

**Conclusions and Future Work**

The aim of this study was to enhance the tribological behavior of glycerol under boundary/mixed lubrication conditions in relatively low sliding conditions and medium loads. Since glycerol has a negative slope in transitioning from static to dynamic friction it will tend to induce stick-slip and shudder behaviour in the system. Therefore, 14 surface active additives where selected for tribological pin-on-disc-testing to see whether they can improve glycerol’s static to dynamic transition behavior or not.

Since the additives disperse better in water, a glycerol water solutions were made. Concentrations of 10 w.t.%; 20 w.t.%; 30 w.t.%; 40 w.t.% and 50 w.t.% of distilled water in a glycerol solution where compared to pure glycerol performance. Distilled water; when mixed with glycerol, reduced the $\mu_1/\mu_{50}$ ratio by half compared to pure glycerol, with the 10 w.t.% and 20 w.t.% outperforming the other solutions. It was noticed that dynamic friction tends to increase with increasing water content. This is understandable since water will lower the load carrying capacity of glycerol. However, this effect was stronger after 30 w.t.% water.

The selected 14 additives where then compared using the same tribo-test in a 10 w.t.% water glycerol solution with 1% additive mixed in. The most effective additive was the ionic liquid based additive which can have a positive static to dynamic friction coefficient slope. Another additive which showed a lot of improvement in performance was a phosphor based additive. In this case the ratio was lowered to be slightly above 1. The two selected additives where then further compared in a 20 w.t.% water glycerol solution with 1% additive. This was done to see
how the water influenced the additive behavior. A slight improvement was noticed in the 20 w.t.% water glycerol solution in both additives.

A concentration study was conducted on both selected additives. For the ionic liquid, concentrations of 0.2%, 0.6%, 1%, 2% and 4% were tested in a 20 w.t.% water glycerol solution. It was noticed that the ratio was improved with increasing concentration until 0.6%; after that, the additive concentration seemed to have negligible effect. Another important observation, was that the ionic liquid increased the friction coefficient with increasing concentration even though the ratio does not change.

The same concentration study was conducted with the phosphor based additive with concentrations of 0.6%, 1%, 2% and 4% in a 20 w.t.% water glycerol solution. In this case, there was a clear adverse trend; where, increasing the additive concentration seemed to make the ratio worse. However, 0.6% solution had the best results in all of the previously mentioned cases which is very interesting. This solution also did not have any adverse effect on the friction coefficient.

Finally, a study on the effect of contact angle on the friction behavior was conducted. Several of the additives had their contact angle measured on bronze and steel using the cessil drop method. This was done because it has been previously theorized that when an oil has a lower contact angle, surface active additives perform better. In our case, there was a correlation between both which confirms the theory. However, further investigation is required to insure statistical significance.

In conclusion, the motivation for this study was the reduction of probable adverse effects that occur when a lubricating oil leaks into the environment; particularly when the machinery is operating in marine environments. Glycerol is an interesting biodegradable compound that has promising tribological properties. However, high viscosity, high freezing point and high static coefficient of friction are undesirable behaviors that can be improved by the addition of water and additives. 14 additives were tested for viability in this study, out of which two; ionic liquid and phosphor based additives, were selected for further investigation. Although both additives have performed very well, 0.6% phosphor based additive in 20 w.t.% water glycerol solution had the best performance. However, this study mainly focused on the static to dynamic friction transition behavior of the lubricant and no studies of wear behavior, corrosiveness, oxidation stability and thermal performance have been conducted. These tests will be required to fully characterize the lubricant and also to shed light on the mechanism with which the additive improves the lubricant performance.
References


