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# Formulation and Testing of New Environmentally Acceptable Lubricants (EAL) for Use in Maritime Gear Components

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Norwegian University of  
Science and Technology

# Formulation and Testing of New Environmentally Acceptable Lubricants (EAL) for Use in Maritime Gear Components

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## Preface

This master thesis is the concluding work of my Master of Science Degree in Material science and engineering taken at Norwegian University of Science and Technology (NTNU). The master thesis has been written during spring 2019 at the Department of Mechanical and Industrial Engineering. The master thesis is a part of the NFR founded Eseal project, and I hereby declare that this master thesis is performed independently and according to rules and regulations at NTNU.

I would like to thank my supervisor Nuria and the Eseal project group for advice, guidance, and help throughout the last year. I would also like to thank the PhD. fellows, Hamid and Wahuy at the tribology lab for helping me in the lab, discussion of the results, and problems with solubility.

I would also like to thank my family, and especially Arne for helping me improve my academic writing. Least, but at last I would like to thank Line, Elin, and Martine for all support, discussions, encouragement, cheering, and good times these last five years. My time as a student would not have been the same without you!

Trondheim, 08-06-2019

A handwritten signature in black ink that reads "Mari Gansmoøy Aspnes". The signature is written in a cursive, slightly slanted style.

Mari Gansmoøy Aspnes



## Abstract

In the marine industry the leakage of lubricants into the sea has been a big environmentally challenge. In order to reduce damage to the environment vessels must use environmentally acceptable lubrication (EAL) in all oil to sea interfaces. In these interfaces there is a chance for seawater to enter, it is therefore important that the lubricant can absorb water in the system. Today synthetic esters are commonly used as EALs, but the drawbacks with these are that they hydrolyze in contact water, which can cause problems in the gear components and lead to lubricant failure.

To address this problem the tribological and rheological properties of two possible environmentally acceptable base oils, one polar (glycerol) and one non-polar (polyalphaolefin) with four types of different environmentally acceptable additives were investigated. The additives were one type of carboxylic acid and three types of ionic liquids. The rheological properties of glycerol aqueous solution, PAO, and three types of commercially available EALs were tested. The tribological performances of the solutions were tested with the use of a pin on disk test and the wear tracks were investigated.

The tests showed that glycerol aqueous solutions had difficulty with the solubility of additives and that the amount of water affected this solubility. PAO, on the other hand, showed improved tribological performance with the addition of carboxylic acid. Glycerol showed a higher wear rate on the worn surface compared with water and PAO. The polarity of the two base oils did not influence the frictional performances. However, the results showed that the polarity influenced the wear rate significantly.



## Sammendrag

I marin industri er lekkasje av smøremidler en stor miljøutfordring. For å redusere slik forurensning til sjøvannet må alle fartøy benytte miljøvennlige smøremidler i all olje til sjø grensesnitt. I disse grensesnittene kan sjøvann forekomme og det er derfor viktig at smøremiddelet har evnen til å absorbere vann i systemet. I dag blir syntetiske estere hovedsakelig brukt som base i smøremiddelet. Ulempen med syntetiske estere er at de hydrolyserer i kontakt med vann, noe som kan føre til nedbrytning av smøremiddelet og skade på komponenter i systemet.

I denne studien ble de tribologiske og reologiske egenskapene til to miljøvennlige baseoljer, en polar (glyserol) og en upolar (polyalphaolefin) base med fire forskjellige miljøvennlige additiver undersøkt. Det ble benyttet en type karboksylsyre og tre forskjellige typer ioniske væsker som additiver. De reologiske egenskapene til vannløsninger av glyserol, PAO og tre forskjellige kommersielle EALs ble testet. De tribologiske egenskapene ble testet ved bruk av en "pin on disk"-test og slitasjesporene ble så undersøkt.

De tribologiske og reologiske testene viste at glyserol byr på utfordringer når det kommer til løselighet av additiver og at mengden av vann påvirker denne løseligheten. Friksjonsegenskapene til PAO ble forbedret ved tilsetning av karboksylsyre. Glyserol hadde høyere slitasjevolum enn både vann og PAO. Dette indikerer at polariteten til baseoljen påvirket slitasjeegenskapene hos smøremiddelet. Resultatene viste også at polariteten ikke påvirket friksjonsegenskapene.



## Acronyms

**ADTC** KX 1323

**Amines** 2-(Diethylamino)ethanol

**API** American Petroleum Institute

**BL1232EL** NA-LUBE BL-1232 EL

**BMP** 1-Butyl-1-methylpyrrolidiniumtris(pentafluoroethyl)trifluorophosphate

**CA** Carboxylic acid

**CoF** Coefficient of Friction

**C12** Lauric acid

**EAL** Environmentally Acceptable Lubricant

**EPA** Environmental Protection Agency

**HEES/PAG** Polyalkylen glycol

**HEPG** Synthetic esters

**HEPR/PAO** Polyalphaolefin

**HETG** Vegetable base fluids

**PC** Trihexyltetradecylphosphonium decanoate

**PP** Tributyl(methyl)phosphonium dimethyl phosphate

**VGP** Vessel General Permit

**VI** Viscosity Index

$R_a$  Average roughness

$R_q$  Root mean square roughness/surface roughness

$h$  Film thickness

$\eta$  Dynamic viscosity

$\nu$  Kinematic viscosity





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# Chapter 1

## Introduction

In the marine industry the leakage of lubricant into the sea has been a big environmentally challenge. The total amount of leaked lubricating oil worldwide is estimated to be between 37 to 61 million liters each year. Lubrication leakage distributes about 10% of the total volume of the sources that cause oil pollution in the marine environment. This is described in figure 1.1, where the lubricant leakages are put in perspective with other coastal and marine-based sources [1].

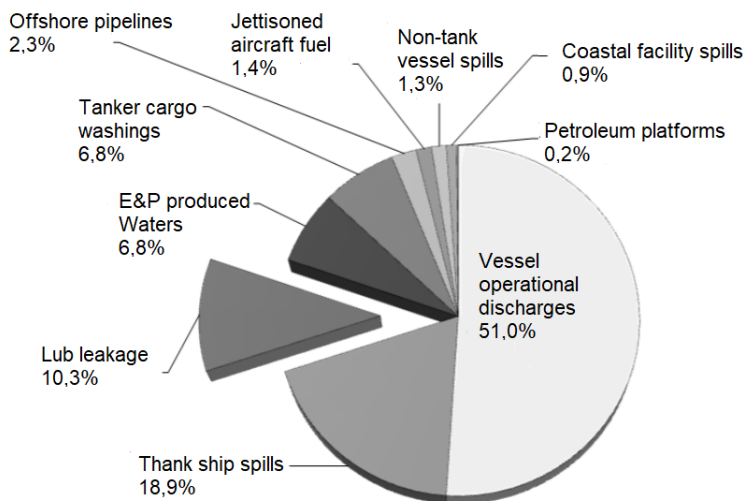


Figure 1.1: Oil inputs into the marine environment [1].

After one and a half century of using petroleum-based oil, people in general have become aware of the comprehensive pollution caused by oil and oil products. In order to preserve the environment and the ecosystems, at land and at sea, there is an increasing focus on reducing the utilization of mineral oil. Concerning the marine industry, the United States Environmental Protection Agency (EPA) enforced the Vessels General Permit (VGP) in 2013 [9]. The VGP states that vessels longer than 37 meters entering the US coast must use an environmentally acceptable lubricant (EAL) in all oil to sea interfaces. EALs are lubricants that are biodegradable, minimally toxic, and non-bioaccumulative. The VGP also defined EALs as products labeled by some of these programs: Blue Angel, European Ecolabel, Nordic Swan, the Swedish Standards SS 155434 and 155470, OSPAR, and DfE. These programs represent a label that defines the products environmental excellence and that the products reach a high environmental standard throughout their life cycle [10]. Lubricants leaking from a vessel will enter the aquatic environment, and they can damage the aquatic ecosystem. Earlier mineral oil was the most used lubrication in the oil to sea interface until VGP introduced with new regulations. Mineral oil is highly toxic and is not biodegradable.

## **1.1 Motivation/objective of the master thesis**

Most of the EALs today are based on synthetic esters. Synthetic esters bring many challenges when it comes to compatibility with seals and interaction with other media as for example water. Because EALs are used in the oil to sea interface, it is important that the lubricant can absorb water, so water can't contaminate the lubricant. This makes synthetic esters not suitable for use in applications where water can contaminate the lubricant since formation of acid will occur. The motivation for this master thesis was to formulate and test an EAL that had better properties than EALs based on synthetic esters. The new formula should be able to absorb more water than the reference lubricant, and the lubricant should have improved tribological properties such as friction and wear performance.

### **1.1.1 Limitations**

Since there are many different types of base oils that can be used to achieve the environmental requirements it has been decided to use one polar (glycerol) and one non-polar (polyalphaolefin) base oil in this master thesis. It was also decided to use the same viscosity as other commercially available lubricants used in gear components, and this viscosity is 68 mPas. It was decided to focus on two to five different additives (friction modifiers, corrosion inhibitors, anti-oxidation, anti-wear, and extreme pressure additives) based on a lubricant used under boundary conditions. These additives were decided to be carboxylic acid and ionic liquids. To be able to investigate and evaluate which one of the base oils and their additives that performed best, tribology and rheology studies of the lubricants were performed.

## 1.2 Tribology

Tribology is the science and technology of interacting surfaces in relative motion to each other. Tribology concerns friction, wear, and lubrication between the surfaces in contact [11]. A typical tribological contact is shown in figure 1.2. A tribological contact can be either lubricated or unlubricated and is affected by different factors such as material parameters, operating condition, environmental conditions, and lubricant properties [2].

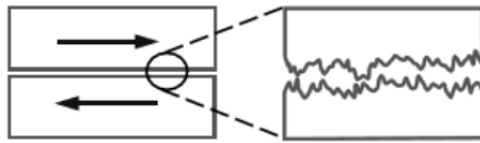


Figure 1.2: Example of a tribological contact [2].

The geometry of the surfaces in contact determines the performance and the operating conditions, and a contact can be either conformal or non-conformal (figure 1.3). In a conformal contact the geometry of the surfaces fits closely together, like for example a concave and a convex surface against each other. The load in a conformal contact is carried out over a large area due to good fit of the geometries. In a non-conformal contact the geometries of the surfaces in contact does not fit each other, such as for example two convex surfaces in contact [2, 12].

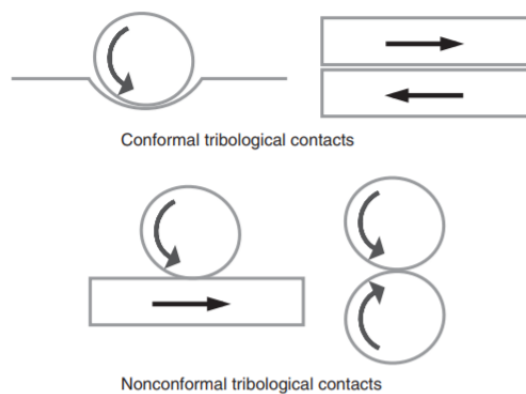


Figure 1.3: Examples of conformal and non-conformal tribological contacts [2].

## 1.3 Lubrication Regimes

A lubricant is a substance used in mechanical parts, and can either be fluid, solid or grease. The lubricant is used in a tribological contact, and the purpose of the lubricant is to separate the moving parts, transfer heat, reduce friction and wear, prevent corrosion, and to transport debris away from the contact. Because the lubricant can separate the surfaces in contact, the film thickness is depending on which regime the lubricant is operating in. There are three different regimes present, i.e. boundary, mixed, and hydrodynamic regime. In boundary regime there is true contact between the asperities of the surfaces in contact, and the lubricant's purpose is to transport the additives to the contacts. These additives will form a film on the surfaces, and this film will reduce wear and friction [2]. In boundary regime the friction and the wear rate are high, and the friction is dominated by adhesion between the asperities and shearing of the lubricant [13].

In mixed regime the asperities on the surfaces will be in contact occasionally. The load will therefore be carried out partly by asperity contacts and partly by fluid pressure [2].

In hydrodynamic regime the film completely separates the surfaces in contact. The separation is created by a positive pressure formed by the surfaces converging, the relative motion and the viscosity [12]. The friction in this regime is due to viscous shear in the lubricant, resistance to hydrodynamic flow, and the surface topography which affects the film thickness [14]. In hydrodynamic regime the purpose of the lubricant is to separate the surfaces completely and reduce friction [2].

### 1.3.1 Stribeck curve

The Stribeck curve shows the evolution of Coefficient of Friction (CoF), film thickness, and wear in the three different lubricating regimes. Figure 1.4 expresses how the CoF, film thickness, and wear behave in boundary, mixed and hydrodynamic lubrication. The figure also contains an indication of which additives that are important in the different regimes. In all regimes friction modifiers are important to decrease friction as much as possible. Anti-oxidants, anti-corrosion

additives, as well as detergents and dispersants are also used in all regimes. In boundary where the asperity contact is high, there is important with extreme pressure and anti-wear additives, since they will control/reduce the wear rate. In hydrodynamic regime are viscosity improvers and anti-foam additives important, to obtain the viscosity and the flow properties of the lubricant.

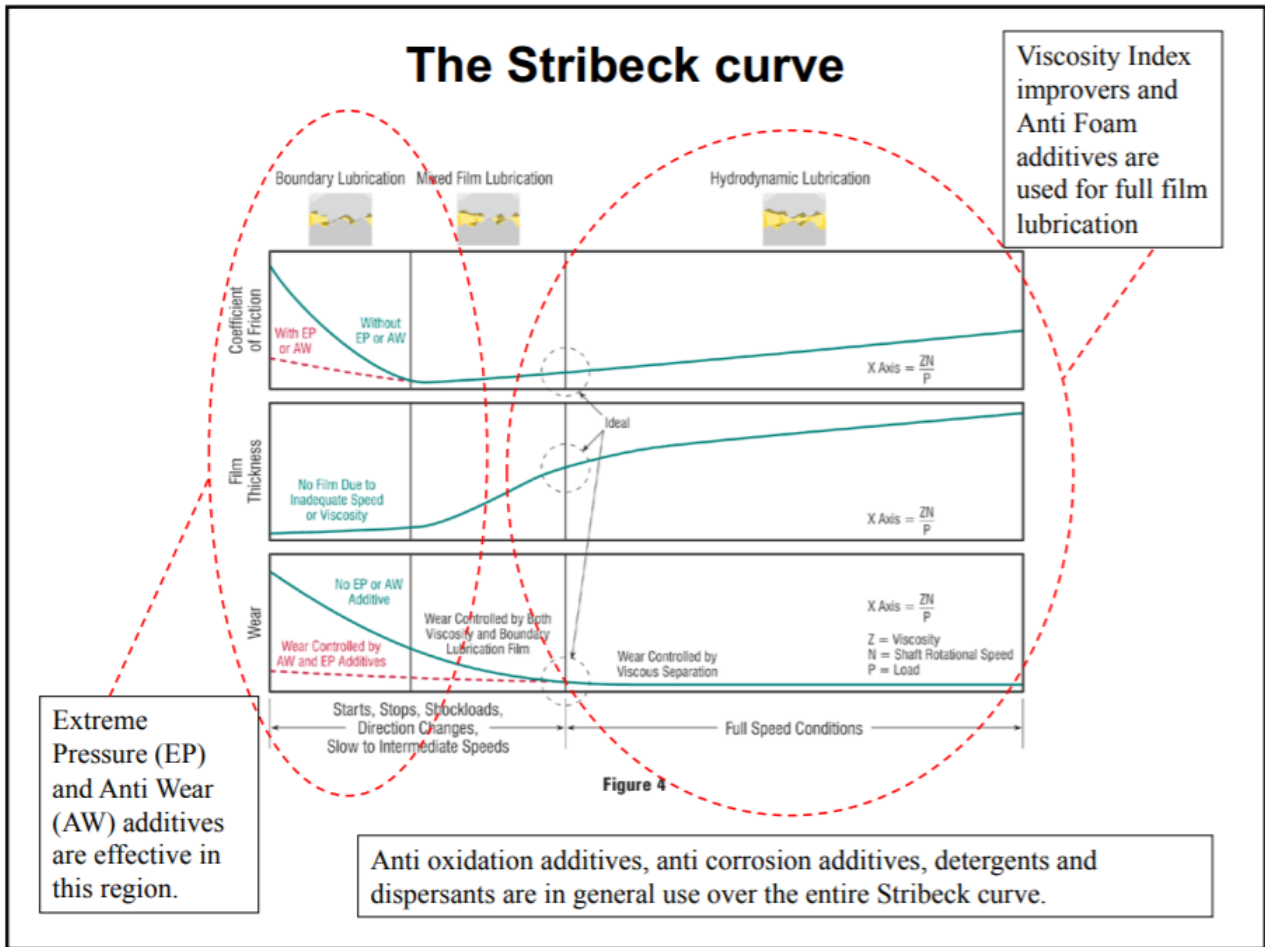


Figure 1.4: The Stribeck curve which expresses how the CoF, film thickness, and wear behave as a function of the three different lubricating regimes, boundary, mixed, and hydrodynamic lubrication. The figure also indicates which additives that are important in the different regimes [3].



## 1.4 Lubricated contacts

Due to their ability to separate surfaces, lubricants are added to tribological contacts to reduce friction and wear. This ability relates on fluid film thickness  $h$  and the surface roughness  $R_q$ . However, the lubricant also contributes to other factors, such as transferring heat, separating the moving parts, preventing corrosion, transporting contaminants or debris away etc. It is important to mention that lubricants reduce adhesive wear, but when it comes to other wear mechanisms, the lubricants are not that effective [2].

### 1.4.1 Rheology of lubricants

A lubricant is designed for different applications and to operate under different conditions. Therefore there are some characteristics of a lubricant that are important to understand, such as viscosity, thermal properties, different long life properties and environmentally properties [2].

#### Viscosity

Viscosity is one of the most important properties when it comes to the performance of the lubricant. It is defined as the resistance to flow of a fluid deformed by shear stress. The viscosity determines the film thickness, and a high viscosity will give a high film thickness. A thin lubricated film will lead to contact between the asperities and hence a higher CoF and wear. On the other hand, a thick film needs more energy to move the surfaces. The viscosity is temperature, pressure and shear rate dependent. At high temperatures the viscosity will decrease, leading to a thinner lubricating film. Viscosity Index (VI) describes the temperature dependency of a lubricant. A lubricant with a high VI has low temperature dependency. When it comes to pressure, an increase will give an increased viscosity. Viscosity can be measured as dynamic viscosity,  $\eta$ , or kinematic viscosity,  $\nu$  [2].

The viscosity can influence the flow properties of a lubricant in two different ways, and the lubricant can be either a Newtonian or a non-Newtonian fluid. A Newtonian fluid is a fluid where the viscosity is independent of the shear rate. A non-Newtonian fluid is a fluid where the viscosity is depended of the shear rate, which means that the fluid does not follow Newtons law

of viscosity (equation 1.1) [15]. As example, glycerol and glycerol aqueous solution behave as Newtonian fluids [16].

$$\tau = \eta \frac{du}{dy} \quad (1.1)$$

Where  $\tau$  is the shear stress,  $\eta$  is the viscosity, and  $\frac{du}{dy}$  is the rate of shear deformation.

Borras et. al [17] studied the rheological properties of EALs, and they found that for PAO and synthetic esters shear thinning could be a problem at high shear rates (above  $10^5 \text{ s}^{-1}$ ). PAO and synthetic esters showed different shear thinning behavior, where PAO tended to have a steady decrease of viscosity, and the synthetic esters showed a sudden decrease of viscosity at high shear rates. The study related the shear thinning to type and amount of the viscosity index improvers used in the lubricants, because the shape, size, and interaction of the polymer chains in the VIIs used in the different formulations act different. In another study by Zopler et. al [18] PAO was described as a fluid with Newtonian flow characteristics, where the film thickness is following the Hamrock-Dowson equation (1.2) with a slope of 0.67. However, shear thinning occurred in PAOs with higher molecular masses.

$$h = kU^{0.67}\eta_0^{0.67}\alpha^{0.53} \quad (1.2)$$

## 1.5 Environmentally acceptable lubrication

A lubricant consist of 70-90% base oil, and the remaining amounts consist of additives. The base oil can be mineral, synthetic or re-refined, where mineral oil is the most common used. Mineral oils consist of hydrocarbons, and they are not classified as EALs by the VGP. The VPG introduced environmentally acceptable lubricants as lubricants with eco-friendly characteristics, such as biodegradability, low toxicity and not being bio-accumulative [9].

### 1.5.1 Classification of base oils

The base oil is the main ingredient of the lubricant and can be divided into synthetic base or mineral oil. Base oils are categorized by American Petroleum Institute (API) where the base oils are divided into five groups, where group IV and V are the synthetic groups. Group IV includes the PAO and group V includes non-synthetic PAOs, such as diesters, polyol esters, alkylated benzenes, phosphate esters etc. The different groups are divided into polar and non-polar synthetic base oils [19]. Polar lubricants have higher affinity to the metal surfaces which may limit the amount of additive molecules on the surfaces, leading to a decreased ability for the additives to produce and form a protective reaction layer on the surfaces. As a result of thinner protective reaction layer, the wear rate can be higher with polar lubricants compared to non-polar lubricants [20]. The polarity and the chemical structure of all base oils varies significantly. PAOs and mineral oils are hydrocarbons, and due to the missing oxygen groups, they have less polarity than synthetic esters (figure 1.5) [4].

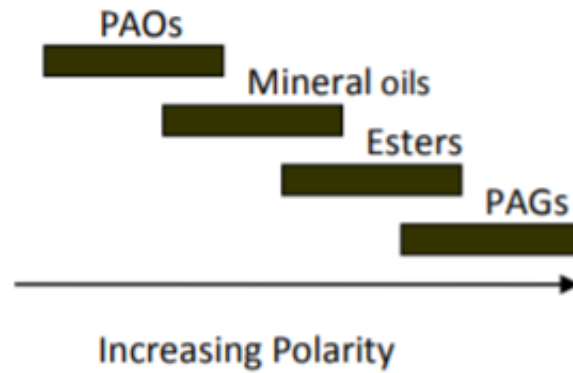


Figure 1.5: Base oils placed with respect to their increased polarity [4].

When it comes to the environmental aspects, an EAL base oil must fulfill the eco-friendly requirements which is set by VGP and the different eco-labels, and because of these requirements mineral oil can not be used as base oils for EALs. Mineral oil will therefore not be discussed in more detail in this thesis. In general, VGP categorized EALs as [21, 22]:

- HETG- vegetable based fluids. Readily biodegradable, suited for dry and cool conditions. When it comes to disadvantages, vegetable oils provide inherent properties which limits the performance of the lubricant. They can suffer from oxidation when exposed to heat, thus limiting the lubricant life. Vegetable oils can also become unstable in contact with water or wet environments.
- HEPG- synthetic esters. Readily biodegradable, good oxidation stability and most common used EAL. Disadvantage when it comes to hydrolysis in contact with water, and when it comes to compatibility with seals. They also perform best under dry and cool conditions such as HETG.
- HEES- polyalkylene Glycol (PAG). PAGs are polymers from petrochemical origin, and they have the ability to resist flame and absorb water. They have a disadvantage when it comes to the solubility of additives, compatibility with materials, and the absorption of water can create rust and wear.
- HEPR- polyalphaolefin (PAO). Fluids derived from PAO base, such as bio-olefin. They do not hydrolyze, and have good properties in wet and hot conditions. They are also com-

patible with several common elastomers.

Polyalphaolefin (PAO) is not listed as an EAL base oil in the VGP. However, new studies have shown that low viscosity PAOs are biodegradable [17, 23] and therefore can be a choice. Also in ISO 15380 PAO partly mixed with esters is classified as a biodegradable hydraulic fluid [24]. Glycerol on the other hand, is not listed as an EAL in any of the eco-label standards. However, glycerol is used as a lubricant in the food industry, they are water soluble and non-toxic, and can therefore be evaluated as an possible base oil.

### **Polyalphaolefin**

PAO is a synthetic hydrocarbon with short molecular length and low side branches, giving the lubricant more consistent properties than for example mineral oil. PAOs general formula is  $C_nH_{2n+2}$  (figure 1.6), and they are composed of hydrogenated olefin oligomers. They are typically produced by a polymerization process of 1-decene, and can consist of a blend of trimer, dimer and tetramer. The olefins consist of double-bonds between the first and second carbon in the hydrocarbon chain [18]. PAOs have good thermal and oxidative stability, low volatility, and high VI. On the other hand, PAOs are non-polar and they can lead to hardening and shrinking of seals [25].

Due to the fact that PAO is non-polar, the solubility of additives might be limited. Taking into account that the additives must also be biodegradable and environmentally friendly, the lack of polarity of PAO limits the number of additives that can be used. Multiple studies suggest that mixing synthetic esters with PAO will increase the solubility of additives and also improve other lubrication properties [17, 22, 25, 26]. However, the addition of esters into the PAO base can reduce certain important properties, such as thermal and hydrolytic stability of the lubricant [27].

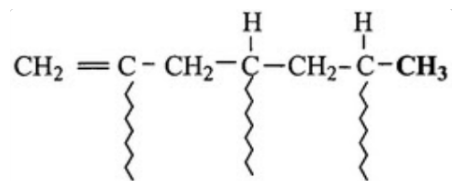


Figure 1.6: Molecular structure of polyalphaolefin [5].

## Glycerol

Glycerol is a trihydric alcohol with molecular formula  $\text{C}_3\text{H}_8\text{O}_3$  and the molecular structure is shown in figure 1.7. The hydroxyl groups are divided into two primary and one secondary group, where the primary groups are more reactive than the secondary. Glycerol is miscible with water and other polar compounds, and is a viscous, colorless liquid and a good solvent due to the hydroxyl groups. This gives glycerol similar solubility characteristics as water etc. However, glycerol can form esters and other derivatives due to the hydroxyl groups. Glycerol is stable to atmospheric oxidation, but can suffer from oxidation by other oxidants [28]. Glycerol also has many other properties such as, hygroscopicity, high flash and fire point, low volatility, non-toxicity, and behaves as a Newtonian fluid. Another important property of glycerol is the high viscosity, and the viscosity can be controlled by addition of water. Pure glycerol has a freezing point at  $18^\circ\text{C}$ , which means that pure glycerol is not suited for use in low temperature. The high viscosity at low temperatures is mostly unwanted due shearing of the lubricant, which leads to energy waste [16]. However, glycerol does not crystallize at low temperatures, but tends to supercool. Addition of water can reduce the freezing point and improve the lubrication behavior of glycerol in the different lubricating regimes [16, 28].

Although the viscosity of glycerol can be controlled by adding water, the lubricating behavior of glycerol aqueous solutions seems to improve with addition of water up to a certain amount. Studies [16, 29] found that solutions with water content above 20 wt% gave a viscosity which was too low to separate the surfaces in contact, due to no formation of a stable film in the contact and poor load carrying capacity. This led to a higher CoF than the mixtures with lower water content, both under boundary and hydrodynamic conditions. Pure glycerol showed less wear loss than the aqueous solutions, indicating that the wear volume increased with increasing wa-

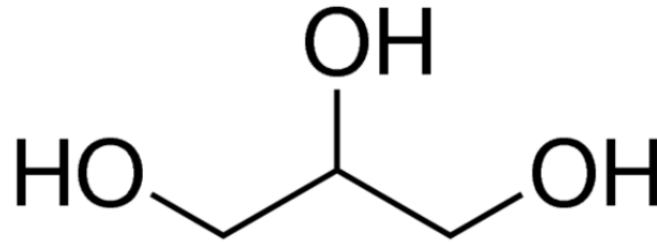


Figure 1.7: Molecular structure of glycerol [6].

ter content. This was due to the decreased load carrying capacity of the lubricant. However, at water content below 20 wt% the wear rate was independent of the CoF. Shi et. al [16] also found that glycerol and glycerol aqueous solutions with water content below 20 wt% had better tribological characteristics than rapeseed oil.

There are few studies on glycerol as a possible lubricant for marine gear components, as an EAL, and glycerol's interaction with additives. However, it has been reported [30] that aqueous glycerol solutions can create structured arrangement of the glycerol and water molecules. This means that free water molecules increases the molecular interactions which establish an easily sheared bearing film between the surfaces. The properties of this water film can reduce the CoF.

### **Tribocorrosion**

Tribocorrosion can act as a wear accelerator when water is present in the system. When using stainless steels which has a passive film on the surface, the degradation mechanism leads to accelerated wear rate. In tribocorrosion systems both mechanical and chemical degradation occur, and the mechanisms interact with each other [31]. Wear accelerated corrosion is a well known phenomenon in literature [32, 33], and is described by the wear will tear off the passive film on the surface of the worn material. When water is present in the system (may be due to use of aqueous lubricants) a galvanic couple is generated, where the worn surface will act as a anode and the un-worn surface will act as a cathode [34].

## 1.6 Additives

Additives are blended with the base oil to give the lubricant improved performance properties. Due to the fact that the main focus in this thesis is the environmental aspect, this also needs to be taken into account when it comes to the additives. The additives are limited due to ecological regulations, which indicates that the formulation should be ashless and only eco-toxicological harmless additives should be used. Due to limitations in this thesis not all types of additives will be discussed in detail.

### 1.6.1 Film-forming additives

#### Friction modifiers

Friction modifiers (FMs) react chemically with the metal surface, leading to the formation of active friction reducing layers. FMs are build up by long, slim molecules with a straight hydrocarbon chain. The hydrocarbon chain consists of a polar head group and a long non-polar chain as shown in figure 1.8. FMs often compete with other types of polar additives with affinity to the metal surface, for example dispersants, detergents, or anti-wear/extreme pressure additives. This can influence the properties of the FMs due to competition of the activation sites. Contaminations in the lubricant, as well as the type of metal surface and the concentration of the FMs are also important factors which are important to control.

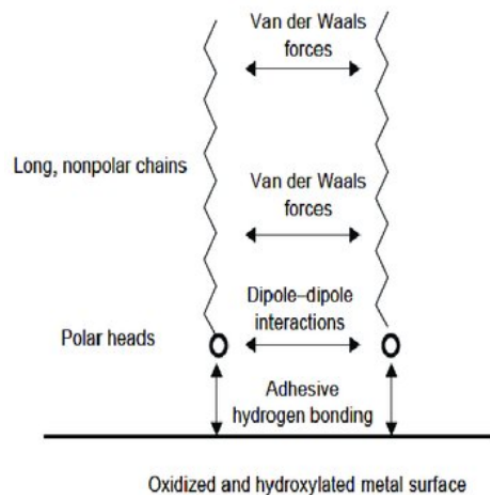


Figure 1.8: Organic friction modifiers and their formation of adsorbed layers [7].



The type of FMs can be divided into four groups based on their mode of action. These four groups and their products are listed in table 1.1:

Table 1.1: Types of friction modifiers based on their type of mode and their products

Mode of action	Products
Formation of reacted layers	Saturated fatty acids, phosphoric acids, sulfur-containing acids
Formation of adsorbed layers	Long-chain carboxylic acids, esters, amines, amides, imides
Formation of polymers	Partial complex esters, methacrylates, unsaturated fatty acids, sulfurized olefins
Mechanical types	Organic polymers

**Formation of reacted layers** are protective layers formed by a chemical reaction between the additive and the metal surface. The reaction should occur in mixed regime, since the chemical reaction should happen under mild conditions. **Formation of adsorbed layers** occurs because the polar head gets attached to the metal surface, and the non-polar hydrocarbon tail is soluble in the oil. All molecules line perpendicular up to the metal surface due to hydrogen bonding between the polar head and the surface. There is dipol-dipol bonding between each polar head attached to the surface and Van der Waals bonding between each hydrocarbon tail. These layers are easy to shear at the hydrocarbon tail, which leads to low friction properties. The properties of the FM adsorbed layers are influenced by the polar group, the chain length, the molecular configuration and the temperature. **Formation of polymers fluid films** occurs due to influence of load and temperature at the contact point. The polymer is developed at the interface between the asperities without a chemical reaction with the metal surface. When it comes to the **mechanical types**, the formation of easy shear layers and the formation of elastic or plastic layers on the metal surfaces leads to reduction in friction. Common mechanical types is molybdenum disulfide, molybdenum and copper compounds, graphite, boron nitride and teflon. The mechanical types is often organic polymers [7].

### 1.6.2 Anti-wear and Extreme pressure additives

The main function of anti-wear (AW) and extreme pressure (EP) additives is to reduce wear in applications with high contact pressure. It is difficult to separate AW and EP additives, however AW additives are designed to produce protective surface films under normal conditions, and EP

additives are designed to operate under more severe conditions. AW can both react chemically with the metal surface or deposit different types of protective films on the surface to reduce wear. For example, hydrodynamic films can hinder asperity contact by producing a thick multilayer film. Other types of protective deposits are monolayer films which reduce shear stress locally at the asperities. On the other hand, EP additives will prevent adhesion or welding between the surfaces in contact. EP additives react with the surface and forms a metal compound. They have a higher film formation rate than AW and produce a thicker and more rougher film compared to AW.

FMs and AW/EP additives can be difficult to separate in boundary conditions. The main difference is the mechanical properties of the AW/EP and FM films. AW/EP films are difficult to shear off due to the fact that the films consist of semi-plastic deposits. These deposits are strongly bound to the surface during sever load in boundary conditions, and the deposits will reduce damages of the asperities. So, due to the difficulty concerning the shearing of this film the CoF will be moderate to high under these conditions. FM films are loosely adhered, closely packed arrays of multimolecular layers, which are connected to the metal by the polar heads. The outer layers can therefore be easily sheared off, leading to a low CoF [7].

### **1.6.3 Contamination and oxidation control additives**

Contamination and oxidation control additives include the anti-oxidants, dispersants and detergents. The main function of these additives is to stabilize and to control the deposit-forming species in the lubricant.

#### **Oxidation Inhibitors**

Oxidation of the lubricant leads to degradation of the oil, due to formation of reactive chemical species, typically radicals. The radical chemical species can lead to changes in the properties of the lubricant, such as viscosity, deposit formation, and corrosion. This process is called oxidation, and is common in hydrocarbon-based lubricants. Since the base oil composition influences the oxidation stability of the oil, studies in general have shown that saturated hydrocarbons are more stable than unsaturated. It is therefore important to obtain a good oxidative

stability of the lubricant, and due to this all lubricants contain at least one anti-oxidant additive.

As already explained anti-oxidant additives protect the lubricant from degradation. The oxidation can be controlled by two main approaches where the first one includes destruction of alkyl radicals, alkyl peroxy radicals, and hydroperoxides. The second approach includes trapping of catalytic metal impurities. The anti-oxidants are divided into primary or secondary anti-oxidants, where primary includes radical scavengers which functions by interrupting the radical chain mechanism of the oxidation reaction. The secondary anti-oxidants include peroxide decomposers, which reduce hydroperoxides in the radical chain to non-radical alcohols.

#### **1.6.4 Biodegradable additives**

The additives can influence the environmental properties of the lubricant, and it is therefore important to have control over which additives that are used. The new restrictions limits the use of certain chemicals as additives, such as zinc, phosphor, sulphur or chlorinated additives [34]. Therefore new types of additives must be investigated and Rudnick [7] stated that ashless AW/EP additives present could improve the environmental effects of the lubricant. Ashless AW/EP additives are non-metallic compounds and the lubricant must have a limited ash content [35]. Since PAO is a non-polar compound and glycerol is a polar compound the solubility of additives will be different in these two base oils, and therefore the solubility of the additives must be taken into account. For example, can ashless additives have better solubility in polar compounds than in non-polar. When it comes to contamination and antioxidation control additives metal-containing additives as sulfur, phosphorus etc. are often not EAL approved due to soot emission and formation of  $\text{SO}_2$  or  $\text{NO}_x$ , however this is regulated by the total amount of additives in the lubricant. ZDDP is the most widely used additive, because it is providing excellent antioxidation and AW/EP properties. It is therefore important to mention that ZDDP are not EAL approved, due to the fact that ZDDP can decompose and form volatile phosphorus species which can be harmful over time.

New additives containing boron, nitrogen, and metal-organic compounds have been studied as potential environmentally friendly additives. For example, organic borate esters show good

AW/EP properties in PAO. However, the borate esters have great affinity with oxygen and is an electron-deficient element. This means that the borate esters are susceptible to hydrolysis, which is an unwanted property for EALs used in marine applications [36]. Studies [37, 38] show that synthesizing the borate ester with an aromatic group and nitrogen, or synthesizing with TPBTL or TBPT will improve the hydraulic stability for a limited time. Organic molybdenum has the same effect as ZDDP, and can reduce both friction and wear due to presence of MoS<sub>2</sub> in the interface [39].

### **Ionic Liquids**

Ionic liquids (ILs) are a relatively new class of salt-based additives with melting points lower than 100°C. ILs are commonly used as green additives due to their excellent physicochemical properties, such as high thermal stability, non-flammability, miscibility with water and organic solvents, and their electrochemical properties. ILs usually contain phosphorus or nitrogen and a weak coordinating anion, which give the compound a unique dipolar structure. The structure can be easily adsorbed on the tribological surfaces in frictional pairs, which leads to formation of a beneficial boundary film. The chemical and physical characteristics of ILs can also be tuned by changing the anion-cation combination, which gives ILs great properties for specific applications. ILs provide excellent friction reduction and anti-wear performance, as well as good load carrying capacity [40, 41]. ILs have many positive benefits, such as no vapor pressure and good thermal stability. This is due to Coulombic or electrostatic forces between the IL molecules. Due to the fact that these forces are much stronger than Van der Waals forces, ILs can behave in a different way than other hydrocarbon-based additives [42].

Compared to conventional oils ILs can limit the amount of additives due to enhanced performance qualities [43]:

- Anti-oxidants can be avoided due to good solvency of the ILs.
- Defoamers can be avoided due to ILs low vapor pressure.
- Anti-wear additives can be avoided if the formation of surface films is present.

- Detergents are not necessary because ILs act as solvents.

In non-polar lubricants polymeric ionic liquids show improved tribological properties, and achieve similar effects as ZDDP [44].

### **Carboxylic acid**

Carboxylic acid (CA) provides good friction reduction properties due to formation of low shear strength films, high mobility, and affinity to the steel surface. They can physisorbed or chemisorbed to the surface depending on the sliding conditions. The low shear strength films prevent contact between the two sliding surfaces by generation of easy slip plane consisting of a mono- or multilayer assembly, thus, reducing the frictional force in the contact. According to literature, micelles can be formed in aqueous solutions with CA [45]. Hence, it is important to notice the critical micelle concentration (CMC) of 0.5 wt% for CA. The formation of micelles occurs due to absorption of surfactants when water is present. These surfactants films can reduce the frictional force, and in water the reduction of friction is due to formation of tightly bound hydration layers also called hydration lubrication [46].

CA are organic compounds with general formula R-COOH (been R a hydrocarbon chain), and the length of the hydrocarbon chain (R) can vary. The length of the hydrocarbon chain corresponds to the coverage of the steel surface, such as a longer tail lead to a larger coverage of the surface. In polar lubricants and in non-polar lubricants the length of the hydrocarbon chain has the same effect when it comes to the surface coverage. However, in polar lubricants the solubility of CA decreases with increasing length of the hydrocarbon chain length. In a lubricated system the length of the hydrocarbon chain influences the tribological performance, thus, the longer chain length the improved performance.

The friction mechanism of CA behaves different in polar and non-polar lubricants. In non-polar lubricants formation of multilayers is promoted, due to high solubility of the hydrocarbon chain. In polar lubricants (typically water-based) the formation of micelles and formation of a thicker multilayer arrangement is prompted. This thicker multilayer leads to a more efficient

friction reduction in polar lubricants than in non-polar lubricants [45].

Different types of CA reacts with different types of modes of action. For example, stearic acid and lauric acid use different modes of action as explained in section 1.6.1. The friction reduction mechanism for stearic acid is promoted by formation of reacted layers, compared with lauric acid and other types of carboxylic acids which is promoted by formation of adsorb layers [47].

## 1.7 Lubricant failures

Failure of the lubricant is important both when it comes to the environmentally aspect and when it comes to problems related to the degradation of a lubricant in an application. Lubricant failures occur due to [34]:

- Contamination of the lubricant
- Change of chemical structure
- Viscosity change

The biodegradability of an organic compound depends on the chemical structure. Hence, the biodegradability can differ from one compound to another regardless if they are based on the same base oil. The biodegradability of a lubricant can also change during the life time of the lubricant due to a variety of factors, such as pressure, temperature, humidity etc. All these factors can lead to a change in the chemical structure. When it comes to how the thermo-oxidative degradation affects the biodegradability of the lubricant, the literature shows that PAO can undergo reduction in the biodegradability. However, this reduction does not come as a result of thermo-oxidative changes, but is induced by the operating conditions in the lubricant application [48].

# Chapter 2

## Experimental method

### 2.1 Lubricants and lubricant formulation

#### 2.1.1 Base oils

A polar and a non-polar base oil were used in this master thesis. PAO SpectraSyn 10 from Exxon-Mobile was the non-polar lubricant, and glycerol (purity  $\geq 99\%$ ) from SIGMA-ALORICH was the polar lubricant. The properties of PAO and glycerol are listed in table 2.1. In order to have the same viscosity in both base oils (68 mPas), four different aqueous solutions of glycerol were prepared. This was done by adding 8 wt%-11 wt% of distilled water into the glycerol fluid.

Table 2.1: Properties of PAO [8] and glycerol [6] which were used as base oils.

Property	PAO	Glycerol
Density (g/l)	835	1250
Kinematic viscosity @ 40°C (cST)	66	not specified
Viscosity Index	137	not specified
Flash point (°C)	266	not specified

#### Reference lubricants

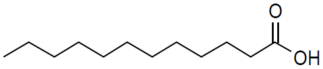
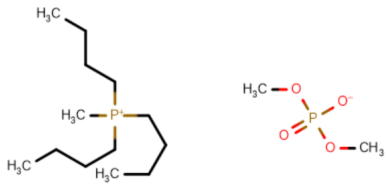
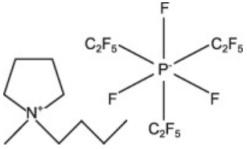
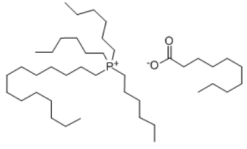
EAL 1 was used as the reference lubricant in rheological as well as tribological testing. EAL 1 is an EAL approved lubricant based on PAO as base oil, and it has a viscosity of 68 mPas at 40°C [49]. EAL 2 and EAL 3 were also used as references in the rheological study. They are both based on synthetic esters, they are EAL approved, and they have a viscosity of 68 mPas at 40°C [50, 51].

### 2.1.2 Additives

One type of carboxylic acid (CA) and three types of ionic liquids (IL) were used as additives in the two different base oils. The chemical formulas and molecular structure of the additives are listed in table 2.2.

Lauric acid (C12) was used as CA, and added in both glycerol and PAO. Due to poor solubility of C12 in glycerol and glycerol aqueous solutions, 0.8 wt % of 2-(Diethylamino)ethanol was added to the solution to increase the pH (above 9) and solubility of C12. It was used the same amount of amine in all glycerol solutions. Tributyl(methyl)phosphonium dimethyl phosphate (PP), 1-Butyl-1-methylpyrrolidinium (BMP) and Trihexyltetradecylphosphonium decanoate (PC) were used as ILs.

Table 2.2: Chemical structure and molecular formulas of the carboxylic acid and ionic liquids.

Additive	Chemical formula	Molecular structures
C12-  Lauric acid	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$	
PP -  Tributyl(methyl)phosphonium dimethyl phosphate	$\text{C}_{15}\text{H}_{36}\text{O}_4\text{P}_2$	
BMP -  1-Butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate	$\text{C}_{15}\text{H}_{20}\text{F}_{18}\text{NP}$	
PC -  Trihexyltetradecylphosphonium decanoate	$\text{C}_{42}\text{H}_{87}\text{O}_2\text{P}$	



### Additive packages

It was used two types of commercial fully formulated additive packages as references in this master thesis:

- NA-LUBE BL-1232 EL (BL1232EL)
- KX1323 (ADTC)

Both packages were delivered from Kings Industries [52] and were approved environmentally friendly additive packages by European Eco label. The eco label states that the maximum amount of both additive packages are 1.8 %. Due to this restriction it was decided to use 1.0 wt% of the additive packages mixed with the base oil to ensure good solubility of the additives.

### 2.1.3 Lubricant formulation

The base oils were mixed with the additives by use of a magnetic stirrer or in a ultrasonic bath (only the ILs) until a homogeneous, transparent fluid was visually confirmed. Due to different solubility of the additive packages and C12 in the two lubricants the majority of the solutions were heated up to around 40°C to increase the solubility of the additives. The lubricant solutions with mixing times and temperatures are listed in table 2.3 for PAO, and in table 2.4 for glycerol.

Table 2.3: The amounts of additives, mixing times and temperatures of PAO solutions.

<b>Base oil</b>	<b>Additives [wt%]</b>	<b>Times and temperatures</b>
PAO	1.0% BL1232EL	10 min, 25°C
PAO	1.0% ADTC	30 min, 40°C
PAO	0.1% C12	1 hour, 45°C
PAO	0.1% PP	45 min
PAO	0.1% PC	30 min

Table 2.4: The amounts of additives, mixing times and temperatures of glycerol solutions.

<b>Base oil</b>	<b>H<sub>2</sub>O [wt%]</b>	<b>Additives [wt%]</b>	<b>Times and temperatures</b>
Glycerol	8% H <sub>2</sub> O		10 min, 25°C
Glycerol	8% H <sub>2</sub> O	1% BL1232EL	30 min, 40°C
Glycerol	8% H <sub>2</sub> O	1% ADTC	30 min, 40°C
Glycerol	8% H <sub>2</sub> O	0.1% C12	45 min, 45°C
Glycerol	8% H <sub>2</sub> O	0.1% C12 0.8% amine	1 hour, 45°C
Glycerol	8% H <sub>2</sub> O	0.3% C12 0.8% amine	1.5 hour, 45°C
Glycerol	8% H <sub>2</sub> O	0.1% BMP	10 hours
Glycerol	8% H <sub>2</sub> O	0.1% PP	30 min
Glycerol	8% H <sub>2</sub> O	0.1% PC	30 min
Glycerol	50% H <sub>2</sub> O		10 min, 25°C
Glycerol	50% H <sub>2</sub> O	0.1% C12 0.8% amine	2 hours, 45°C

In order to investigate the solubility of water in glycerol and the possibility of invisible phases based on pH when amines were added to the solution, a test with pH indicator (phenolphthalein) was performed. The indicator changes color based on pH, and in basic solutions (pH between 8-12) the indicator has a pink/purple color. In neutral and acidic solutions (pH below 7) the indicator is colorless. The pH of all glycerol/C12 solutions were measured.

## 2.2 Testing and characterization

### 2.2.1 Rheological study

The rheological properties of the lubricants were studied by use of HAAKE MARS Rotational Rheometer. First the rheometer was used to achieve the right viscosity of the glycerol/H<sub>2</sub>O solutions. In this master thesis the viscosity was decided to be 68 mPas. Four different glycerol/H<sub>2</sub>O mixtures were tested, with 8 wt%, 9 wt%, 10 wt%, and 11 wt% of H<sub>2</sub>O where the remaining amount was glycerol. The rheological properties of pure PAO and three types of commercially available EAL (EAL 1, EAL 2 and EAL 3) were also studied. The dynamic viscosity of the lubricants was measured at a shear rate from 0 to 500 s<sup>-1</sup> at 40 °C. A lubricant volume of 2 ml was added to the cup and bob cylinder. The force required to shear the fluid was measured in the cylinder where the lubricant was added. The test protocol used can be found in table 2.5.

Table 2.5: Parameters for the HAAKE MARS Rotational Rheometer test.

Step	Shear rate [s <sup>-1</sup> ]	Temperature [°C]	Time [s]
1	0	40	100
2	0.01 → 500	40	180
3	500	40	15
4	500 → 0.01	40	180
5	0.01	40	15
6	0.01 → 500	40	180
7	500	40	15
8	500 → 0.01	40	180
9	0	25	100

### 2.2.2 Tribological tests

To study the tribological performances of the formulated lubricants a pin on disc tribometer was used. The pin on disc tribometer was delivered by Phoenix Tribology. The Coefficient of Friction (CoF) was measured by use of a ball on plate configuration. All tests were performed under boundary conditions, with high contact pressure and low sliding unidirectional velocity. There were performed two tests with the same type of lubricant, and an amount of 1 ml lubricant was added each time. All test parameters are listed in table 2.6.

Table 2.6: Parameters for the pin on disk test.

<b>Parameter</b>	<b>Value</b>	<b>Unit</b>
<b>Test duration</b>	30	minutes
<b>Velocity</b>	0.005	m/s
<b>Lubricant temperature</b>	Room temperature	°C
<b>Load</b>	20	N
<b>Wear track radius</b>	5	mm
<b>Pin diameter</b>	6	mm
<b>Pin material</b>	Alumina (Al <sub>2</sub> O <sub>3</sub> )	
<b>Plate material</b>	SS316	

The steel specimens were cleaned with water and acetone after the pin on disc test.

To study the wear tracks on the worn surface after the pin on disk tests the wear profile and an image of the wear track of each test was extracted by use of an Alicona Infinite Microscope (IFM). Further, the surface profile was inserted into Mountains Map, a software which was used to calculate the wear volume of each sample.

### **Sample preparation**

Preparing of the SS316 steel specimens used in the tribological experiments was performed by grinding and diamond polishing with 3 microns. This was done in order to achieve a homogeneous surface of all the specimen surfaces and to reduce the influence of human error. The grinding and polishing procedures performed are presented in table 2.7.

Table 2.7: The six grinding and polishing steps with SIC paper value used in the sample preparation.

<b>STEP</b>	<b>SIC- PAPER VALUE</b>
<b>1</b>	120
<b>2</b>	220
<b>3</b>	500
<b>4</b>	1000
<b>5</b>	2000
<b>6</b>	3 micron diamondspray



# Chapter 3

## Results

### 3.1 Rheology

The results from the rheological study will be presented by the dynamic viscosity (hereby referred to as viscosity) [mPa] as a function of shear rate [ $s^{-1}$ ] at 40°C, and for glycerol and glycerol aqueous solutions the results are shown in figure 3.1. The figure shows that glycerol had the highest viscosity out of all the solutions that were tested in this master thesis. At shear rates below  $200 s^{-1}$  the viscosity of glycerol decreased from 250 mPas to 165 mPas. From  $200 s^{-1}$  up to  $500 s^{-1}$  the viscosity decreased further down to 147 mPas. Glycerol + 8% H<sub>2</sub>O had less decrease in viscosity with increasing shear rate, and the viscosity decreased from 77 to 57 mPas at shear rates from 50 to  $500 s^{-1}$ . For glycerol + 9% H<sub>2</sub>O the viscosity decreased from 60 to 43 mPas at the shear rates from 50 to  $500 s^{-1}$ . For glycerol + 10% H<sub>2</sub>O the viscosity decreased from 49 to 43 mPas at shear rates from 50 to  $500 s^{-1}$ . For glycerol + 11% H<sub>2</sub>O the viscosity decreased from 60 to 49 mPas at shear rates from 50 to  $500 s^{-1}$ .

The viscosity [mPas] as a function of shear rate [ $s^{-1}$ ] at 40°C for PAO and three commercially available EALs, EAL 1, EAL 2 and EAL 3 are shown in figure 3.2. The figure shows that all four lubricants behaved similar under the conditions used in this rheological study.

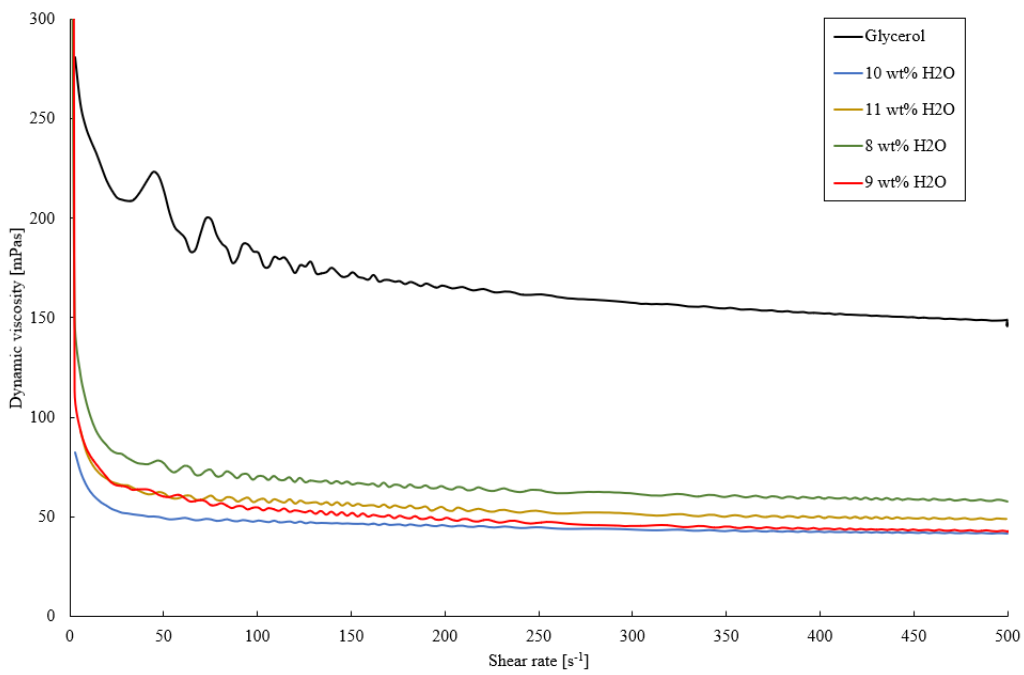


Figure 3.1: Dynamic viscosity [mPas] vs Shear rate [s<sup>-1</sup>] at 40°C of glycerol and glycerol aqueous solutions with 8, 9, 10 or 11 wt% of H<sub>2</sub>O.

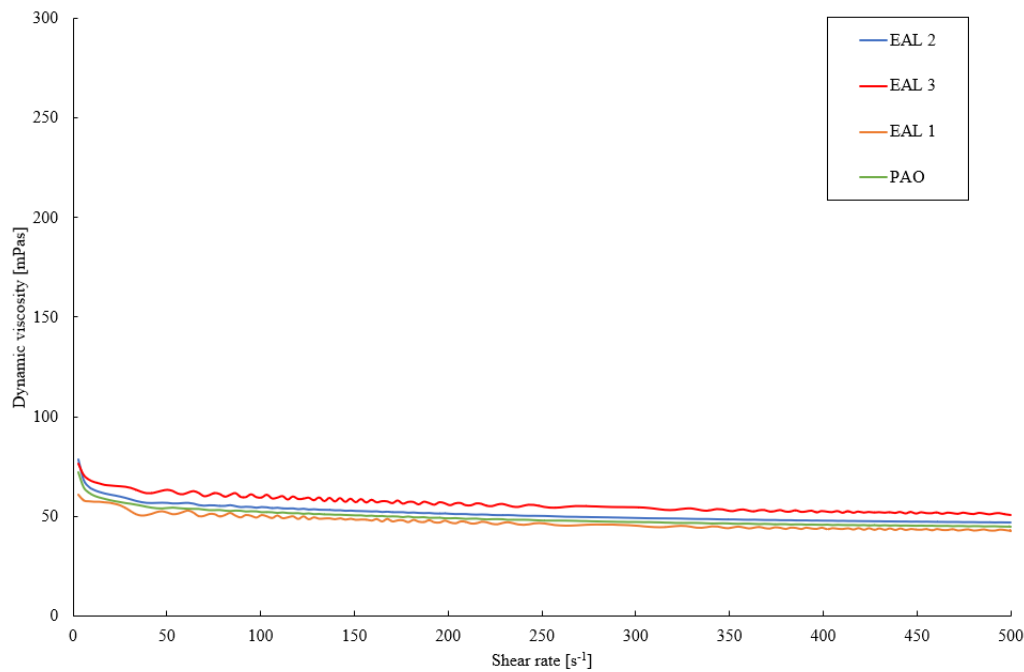
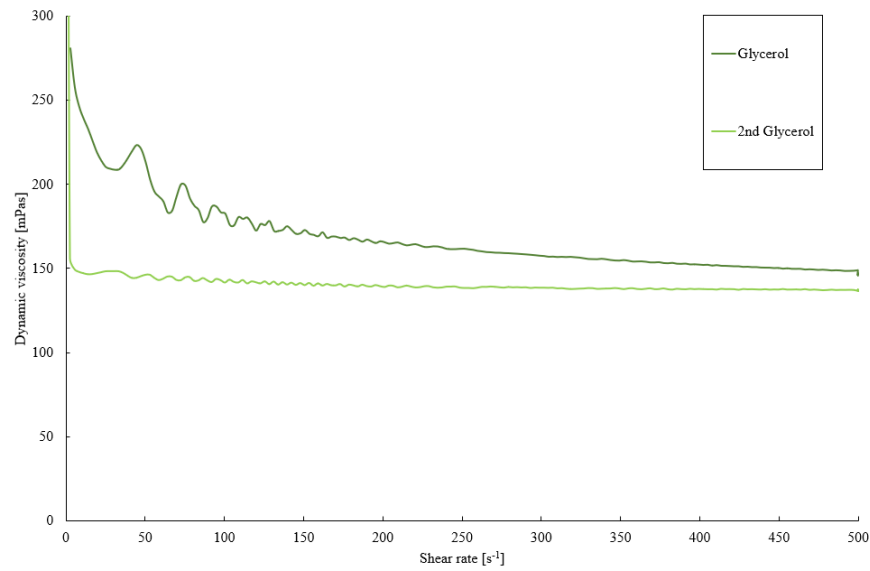


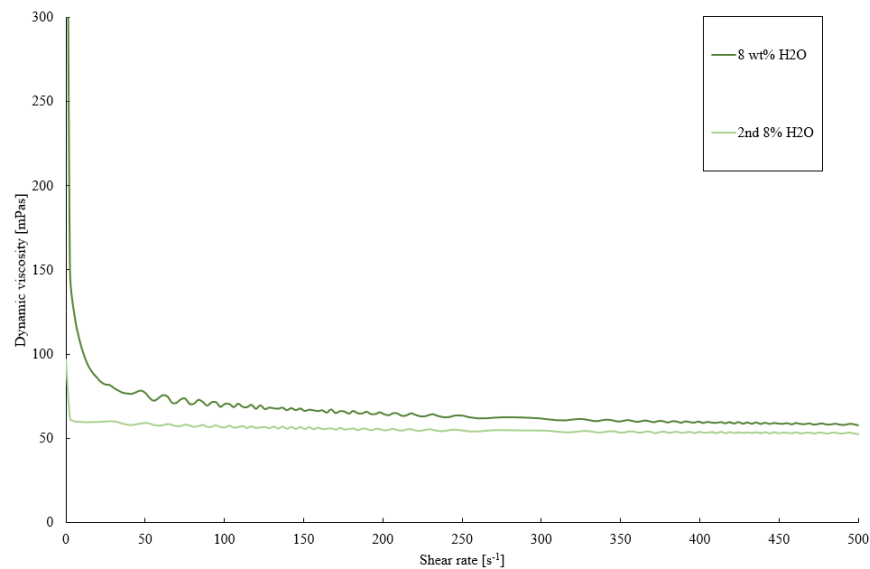
Figure 3.2: Dynamic viscosity [mPas] vs Shear rate [s<sup>-1</sup>] at 40°C of PAO base oil and three types of industrial EAL, EAL 1, EAL 2, and EAL 3 as reference lubricants.



All the rheological tests were performed by running the shear rate up to  $500 \text{ s}^{-1}$  two times (ref table 2.5 in section 2.2.1). The result showed that the viscosity was lower in the second run up to  $500 \text{ s}^{-1}$ , which was a common trend for all the rheological tests. This is shown for (a) glycerol and (b) glycerol + 8%  $\text{H}_2\text{O}$  in figure 3.3.



(a)



(b)

Figure 3.3: Dynamic viscosity [mPas] vs Shear rate [ $\text{s}^{-1}$ ] at  $40^\circ\text{C}$  of (a) glycerol and (b) glycerol + 8%  $\text{H}_2\text{O}$ , including the second increase of shear rate step from  $0-500 \text{ s}^{-1}$ .

The average viscosities [mPas] from both measurements at shear rates between 200 to 500  $\text{s}^{-1}$  at 40°C for PAO, EAL 1, EAL 2, and EAL 3 are presented in figure 3.4. PAO had a viscosity at 45 mPas, EAL 1 at 43 mPas, EAL 2 at 47 mPas, and EAL 3 at 52 mPas.

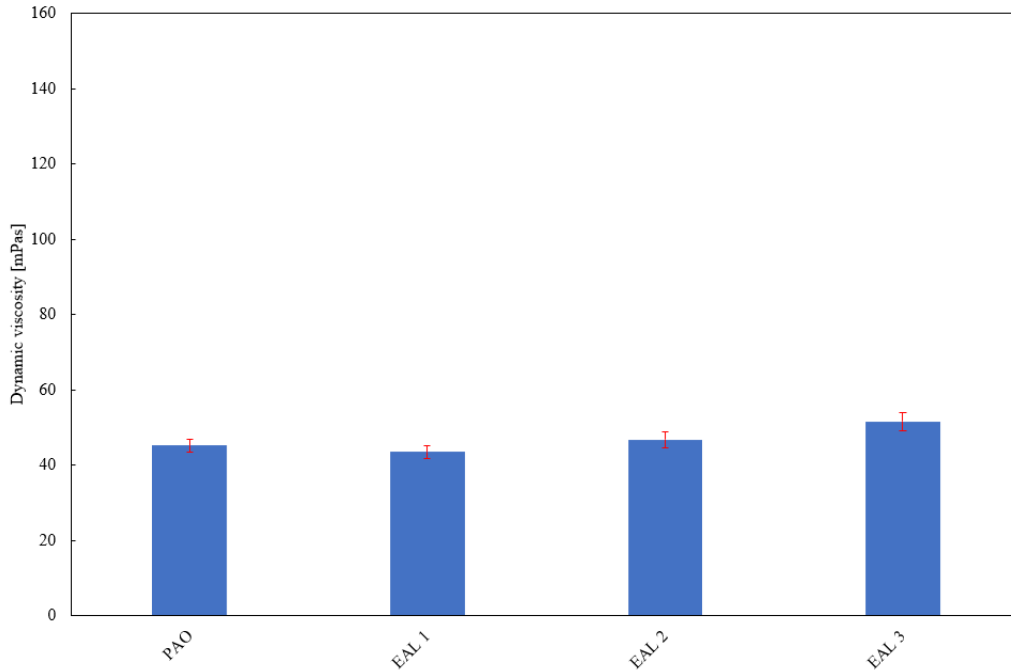


Figure 3.4: The average dynamic viscosity [mPas] for PAO, EAL 1, EAL 2, and EAL 3 at shear rates between 200 to 500  $\text{s}^{-1}$  at 40°C.

The average viscosities [mPas] from both measurements at shear rates between 200 to 500  $\text{s}^{-1}$  at 40°C for glycerol and glycerol aqueous solutions are presented in figure 3.5. Glycerol had the highest viscosity out of all the lubricants that were tested, at 147 mPas. By addition of water the viscosity decreased, and 8% of  $\text{H}_2\text{O}$  gave a viscosity at 57 mPas, 9%  $\text{H}_2\text{O}$  at 43 mPas, 10%  $\text{H}_2\text{O}$  at 42 mPas, and 11%  $\text{H}_2\text{O}$  at 49 mPas.

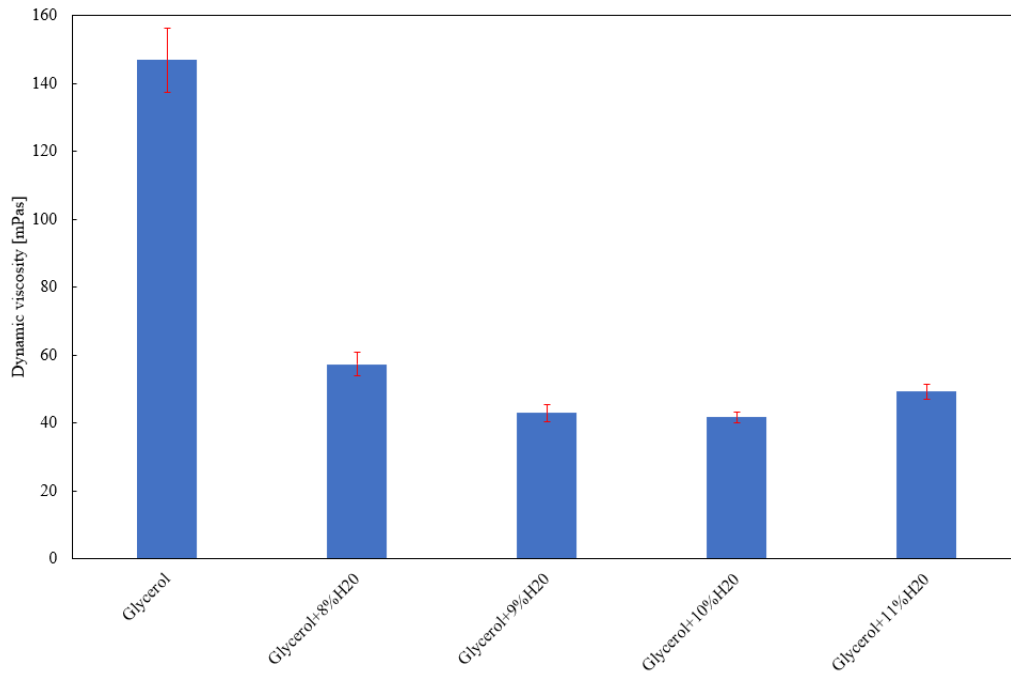


Figure 3.5: The average dynamic viscosity [mPas] for glycerol and glycerol with 8, 9, 10, and 11% of  $\text{H}_2\text{O}$  at shear rates between 200 to 500  $\text{s}^{-1}$  at 40°C.

## 3.2 Solubility of additives

All the results in this section are based on either visual observations or pH measurements.

### In glycerol

BMP was considered not soluble in glycerol, as droplets were observed in the lubricant after 10 hours of mixing. Thus, no further testing was done with this mixture, and the BMP solution will therefore not be discussed any further in this master thesis.

The additive packages were insoluble in the glycerol/H<sub>2</sub>O solution, because of the water present in the glycerol solution [52]. Figure 3.6 shows how the two glycerol solutions with the additive packages looked like after mixing. It was observed a thin yellow layer on top of the glycerol + 1.0% BL1232EL. In glycerol + 1.0% ADTC there was observed a thin transparent layer on top of a sludgy mixture.

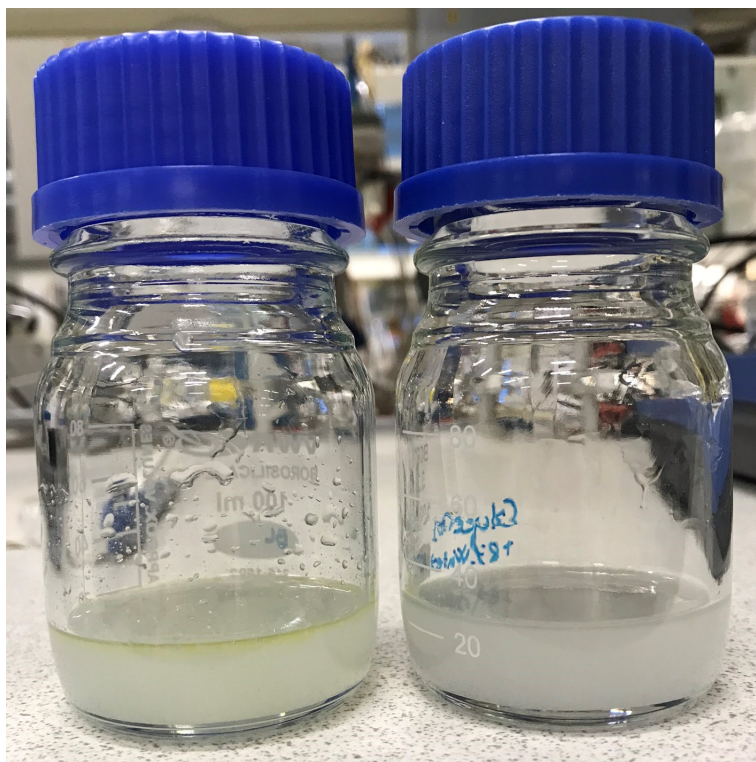


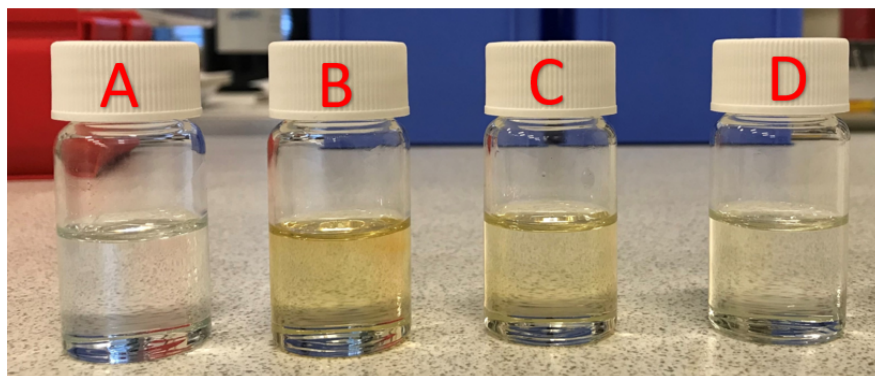
Figure 3.6: Glycerol with 1.0% BL1232EL to the left and glycerol with 1.0% ADTC to the right.

In order to understand how the pH affected the solubility of C12 in glycerol the pH of all glycerol aqueous solutions with C12 was measured. The results are listed in table 3.1. Glycerol aqueous solutions with and without C12 had a pH of 4. These solutions had visual unsolved C12 in the lubricant after mixing. The addition of 0.8% amines increased the pH of all the solutions. 0.1% C12 with amines and 8% H<sub>2</sub>O + 0.3% C12 with amines had a pH of 9.9. 8% H<sub>2</sub>O + 0.1% C12 had a pH of 10.1, and the 50% H<sub>2</sub>O + 0.1% C12 with amines had the highest pH of 10.3.

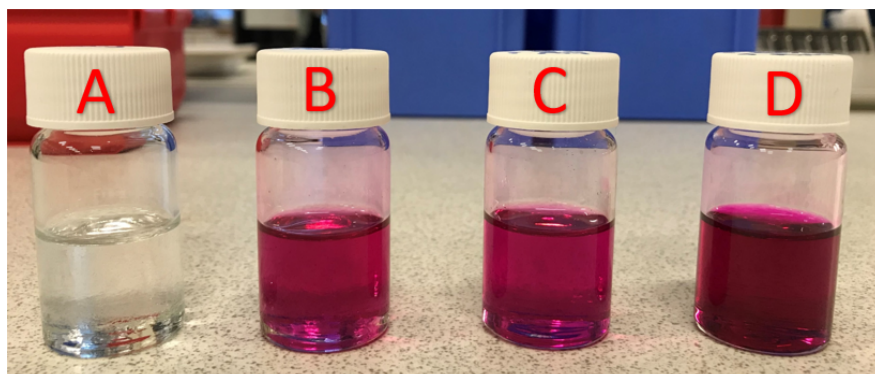
Table 3.1: pH of glycerol and all glycerol aqueous solutions both with and without C12 and 0.8% amines.

<b>Solution</b>	<b>pH</b>
Glycerol + 0.1% C12 + 0.8% amine	9.9
Glycerol + 8% H <sub>2</sub> O	4.5
Glycerol + 8% H <sub>2</sub> O + 0.1% C12	4.4
Glycerol + 8% H <sub>2</sub> O + 0.1% C12 + 0.8% amine	10.1
Glycerol + 8% H <sub>2</sub> O + 0.3% C12 + 0.8% amine	9.9
Glycerol + 50% H <sub>2</sub> O	4.3
Glycerol + 50% H <sub>2</sub> O + 0.1% C12 + 0.8% amine	10.3

To investigate the solubility of water in glycerol and the possibility of invisible phases based on pH when amines were added to the solution, a test with pH indicator was performed. Figure 3.7 shows how the four different tests reacted with addition of phenolphthalein into the solution. Solution (A) is glycerol, (B) is glycerol + 0.8% amines, (C) is glycerol + 0.8% amines + 8% H<sub>2</sub>O, and (D) is glycerol + 0.8% amines + 50% H<sub>2</sub>O. B, C, and D showed a pH above 7, where solution D showed the highest pH by the darkest color of the solutions.



(a)



(b)

Figure 3.7: Detection of phases in four different solutions with help of a pH indicator where (a) are the tests without phenolphthalein and (b) are the tests with phenolphthalein. Solution (A) is glycerol, (B) is glycerol + 0.8% amines, (C) is glycerol + 0.8% amines + 8% H<sub>2</sub>O, and (D) is glycerol + 0.8% amines + 50% H<sub>2</sub>O.

### 3.3 Coefficient of Friction

The frictional performances of the base oils were all tested under the same conditions and are presented as a function of the Coefficient of Friction (CoF) vs. Time [s]. Figure 3.8 shows how PAO, glycerol, glycerol + 8% H<sub>2</sub>O, and H<sub>2</sub>O behaved during boundary conditions at room temperature. H<sub>2</sub>O had a low CoF during the running in period up to 200 s. From this point and up to 600s the CoF increased before it reached steady state. This behavior was not observed in the remaining lubricants. Common for PAO, glycerol and glycerol + 8% H<sub>2</sub>O was a running in period with high CoF in the first 200 s, before the glycerol, and glycerol + 8% H<sub>2</sub>O reached steady state after 200 s. PAO on the other hand, had a small increase in the CoF from 400 s to 800 s, before the CoF stabilized.

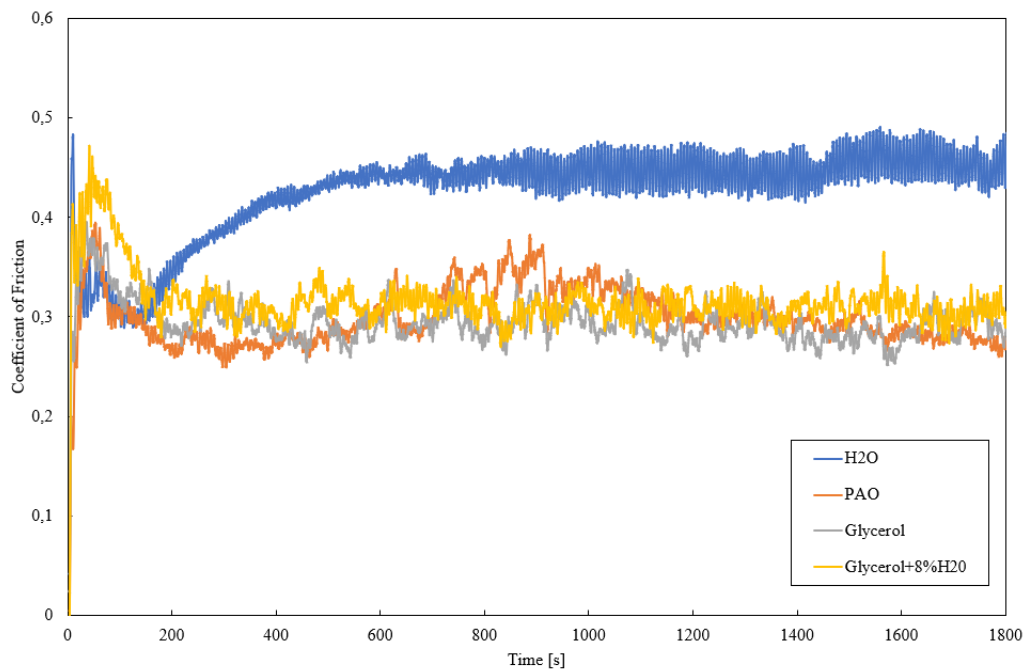
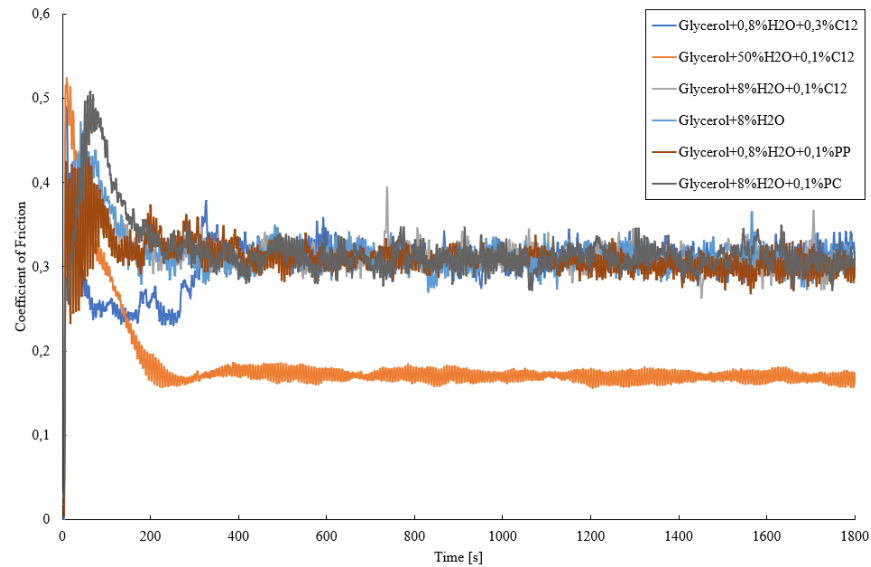


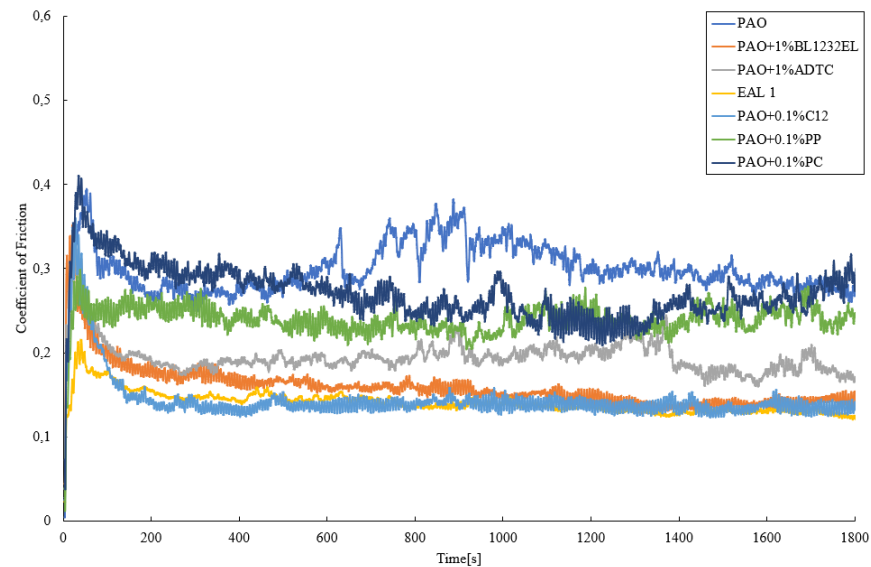
Figure 3.8: Frictional performances of water, glycerol, glycerol + 8% H<sub>2</sub>O, and PAO as a function of time [s]. The tests were performed under 20 N applied to alumina ball and SS 316 at sliding unidirectional velocity of 0.005 m/s at room temperature.

In order to understand the frictional effect of the additives in (a) glycerol and in (b) PAO an additional set of tests were performed (Figure 3.9). In both (a) and (b) all tests had a running in period with high CoF, before the CoF decreased. In (a) the mixture with 50% H<sub>2</sub>O + 0.1% C12 had the lowest CoF in the steady state region (after 200 s). The glycerol + 0.8% H<sub>2</sub>O + 0.3% C12 showed a lower CoF than the other C12 solutions with 8% H<sub>2</sub>O up to 300 s before the CoF reached the same value as the remaining solutions. For the remaining solutions (1.0% ADTC and 1.0% BL1232EL) the frictional performances are presented in the appendix (A.1). The frictional results from use of the additive packages in glycerol are not further discussed in this thesis, as the additives were insolvable in glycerol due to the water present in the solution (data sheet from [52]). In (b) the CoF varied over time after the running in period for PAO, PAO + 0.1% PC, and PAO + 1.0% ADTC. For the remaining three solutions the CoF behaved more stable after the running in period.





(a)



(b)

Figure 3.9: Frictional performances of (a) glycerol solutions: glycerol + 8% H<sub>2</sub>O, glycerol + 8% H<sub>2</sub>O + 0.1% C12, glycerol + 8% H<sub>2</sub>O + 0.3% C12, glycerol + 8% H<sub>2</sub>O + 0.1% PP, glycerol + 8% H<sub>2</sub>O + 0.1% PC, and glycerol + 50% H<sub>2</sub>O + 0.1% C12 (all C12 solutions are containing 0.8% amines), and (b) PAO solutions: PAO, PAO + 0.1% C12, PAO + 0.1% PP, PAO + 0.1% PC, PAO + 1.0% ADTC, PAO + 1.0% BL1232EL, and EAL 1 as a function of time [s]. The tests were performed under 20 N applied to alumina ball and SS 316 at sliding unidirectional velocity of 0.005 m/s at room temperature.

### 3.3.1 In glycerol

Figure 3.10 shows the average CoF in the steady state region for glycerol, H<sub>2</sub>O, and glycerol aqueous solutions. H<sub>2</sub>O had the highest CoF out of all the tests performed independent of which lubricant and additive that were used. The CoF for H<sub>2</sub>O was 0.43, glycerol had CoF of 0.30, glycerol + 8% H<sub>2</sub>O had a CoF of 0.32, and glycerol + 50% H<sub>2</sub>O had a CoF of 0.31.

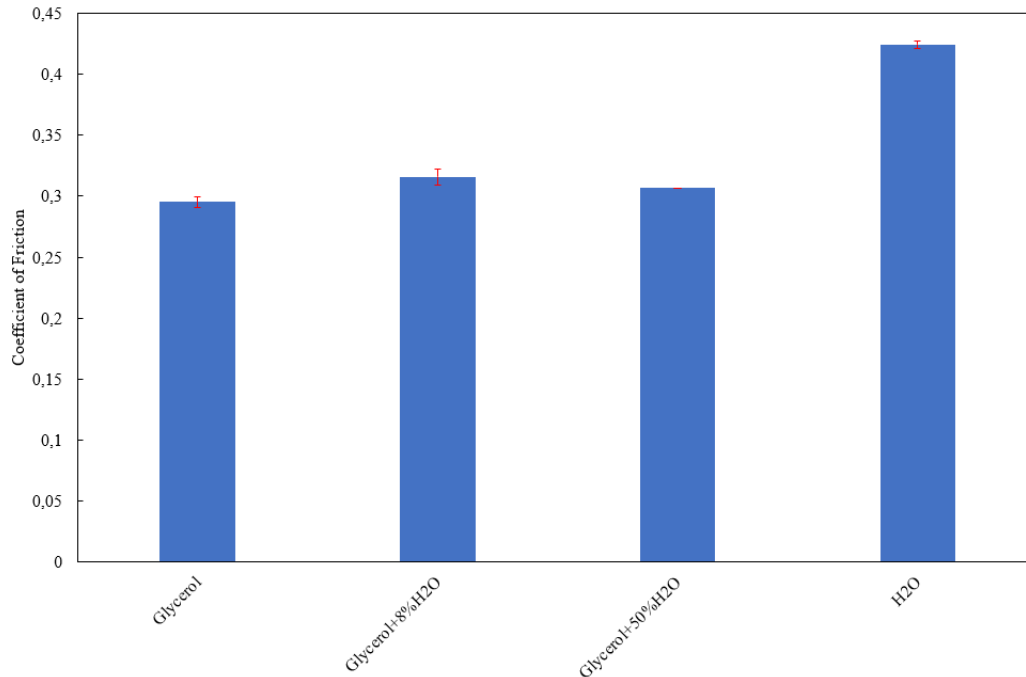


Figure 3.10: Frictional performances of glycerol, glycerol + 8% H<sub>2</sub>O, glycerol + 50% H<sub>2</sub>O, and H<sub>2</sub>O in the steady state period during the tribological test. The tests were performed under 20 N applied to alumina ball and SS 316 at sliding unidirectional velocity of 0.005 m/s at room temperature.

Figure 3.11 shows the average CoF in the steady state region in reference with glycerol for glycerol aqueous solutions (with 8% or 50% H<sub>2</sub>O) and 0.1% of one of the additives C12, PP, or PC. The figure also includes the frictional performance of the tests of glycerol + 0.3% C12. For the solution with 8% H<sub>2</sub>O + 0.1% C12 had a CoF of 0.32, and with 8% H<sub>2</sub>O + 0.3% C12 the CoF was 0.31. The remaining solutions with 8% H<sub>2</sub>O + PP had a CoF of 0.31, 8% H<sub>2</sub>O + PC of 0.32. The solution with 50% H<sub>2</sub>O + 0.1% C12 the CoF was 0.18, which was the lowest CoF out of all the glycerol solutions.

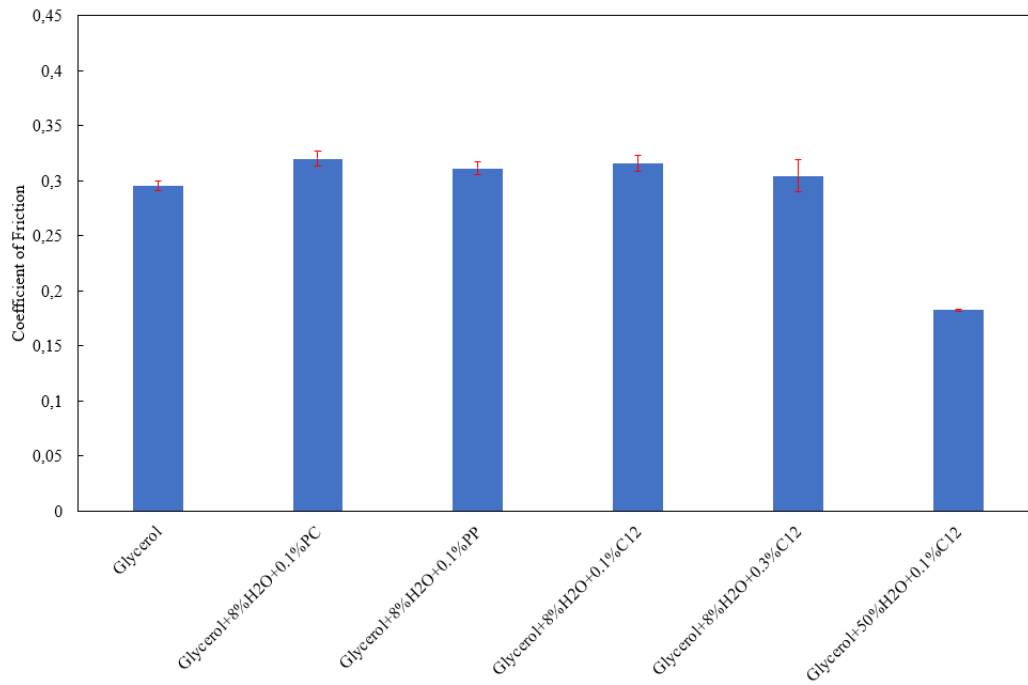


Figure 3.11: Frictional performances of glycerol aqueous solution with 8% and 50% H<sub>2</sub>O, and 0.1% amount of one of the additives PP, PC, C12, or 0.3% of C12 in the steady state period during the tribological test. The tests were performed under 20 N applied to alumina ball and SS 316 at sliding unidirectional velocity of 0.005 m/s at room temperature.

### 3.3.2 In PAO

Figure 3.12 shows the average CoF in the steady state region for the reference lubricant EAL 1 and PAO with the EAL approved additive packages (1.0% ADTC or 1.0% BL1232EL). EAL 1 had a CoF of 0.14. The PAO + ATDC had a CoF of 0.24, and the PAO + BL1232EL had a CoF of 0.16.

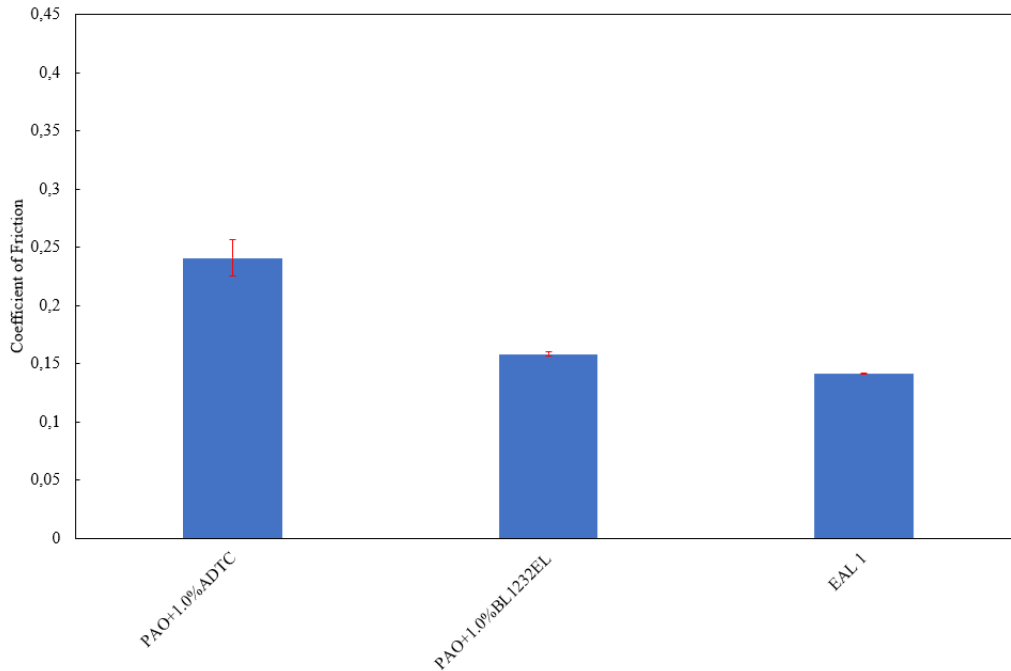


Figure 3.12: Frictional performances of PAO + 1.0% ADTC, PAO + 1.0% BL1232EL, and for EAL 1 as reference lubricant. The tests were performed under 20 N applied to alumina ball and SS 316 at sliding unidirectional velocity of 0.005 m/s at room temperature.

Figure 3.13 shows the average CoF in the steady state region for PAO and the PAO solutions with 0.1% of one of the three different additives C12, PP, or PC. The pure PAO had a CoF of 0.30, PAO + C12 had a CoF of 0.14, PAO + PP had a CoF of 0.24, and PAO + PC had a CoF of 0.27.

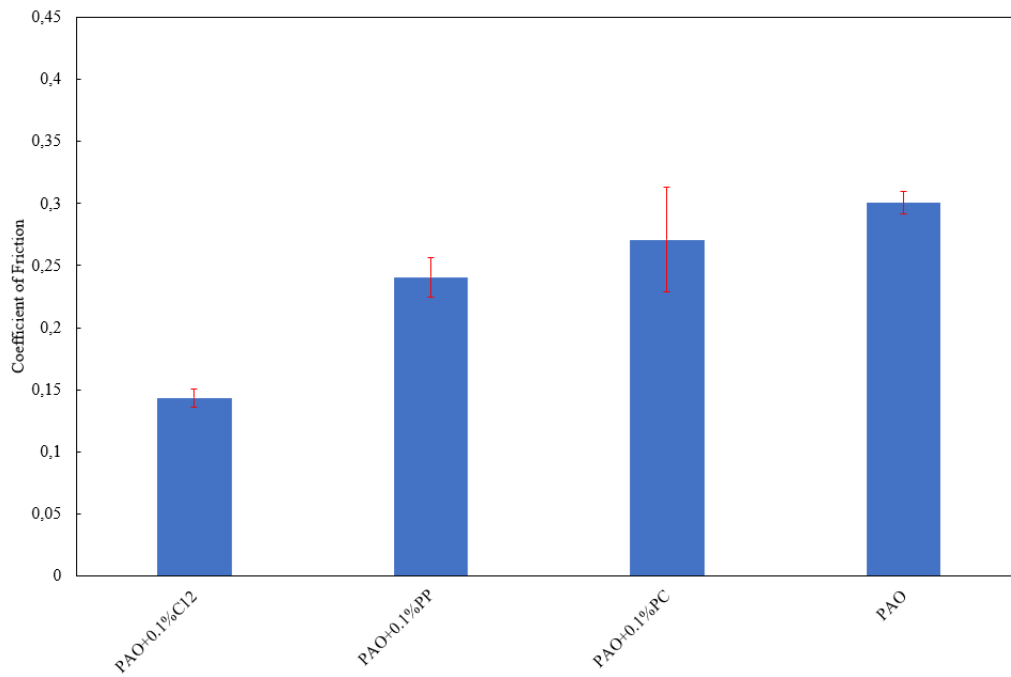


Figure 3.13: Frictional performances of PAO and PAO solutions with 0.1% of one of the additives C12, PP or PC. The tests were performed under 20 N applied to alumina ball and SS 316 at sliding unidirectional velocity of 0.005 m/s at room temperature.

### 3.4 Wear

In order to show how the wear volume was calculated it is presented one example of the surface profile and the wear track. The extracted wear track of the worn surface (SS 316) lubricated with glycerol from the IFM and Mountains Map is presented in figure 3.14. All IFM images in this thesis were taken with a 10X magnification. The surface profile of the wear track from the same test as explained above is presented in figure 3.15. The red area in the figure is further used for calculating the wear volume of each wear track.

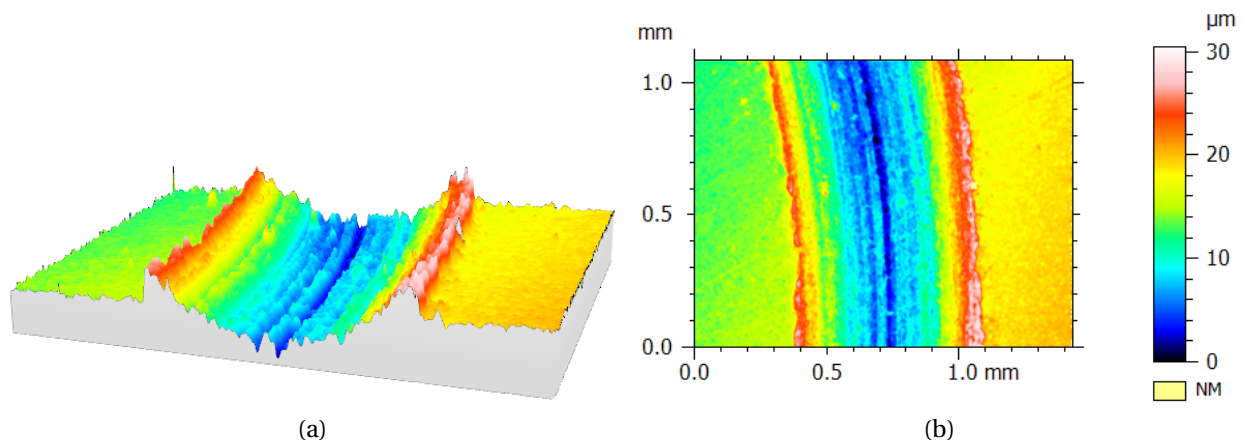


Figure 3.14: Topography image of the wear track of glycerol (a) in a 3D view and (b) from IFM with color scale indicating the differences in height and depth on the surface. 10X magnification.

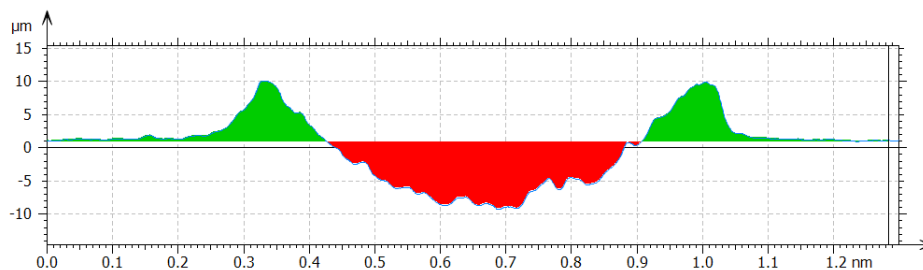


Figure 3.15: Surface profile of the wear track on the worn surface (SS 316) lubricated with glycerol. The red area is the depth of the wear track, and the green area is the collection of wear debris from the wear track.

### 3.4.1 In glycerol

The wear volumes from the tests lubricated with glycerol, glycerol aqueous solutions, and H<sub>2</sub>O are presented in figure 3.16. The wear volume of glycerol was 0.050  $\mu\text{m}^3$ , of glycerol + 8% H<sub>2</sub>O was 0.037  $\mu\text{m}^3$ , of glycerol + 50% H<sub>2</sub>O was 0.007  $\mu\text{m}^3$ , and for H<sub>2</sub>O it was 0.005  $\mu\text{m}^3$ , which was the lowest wear volume out of all calculated wear tracks independent of which lubricant and additives that were used.

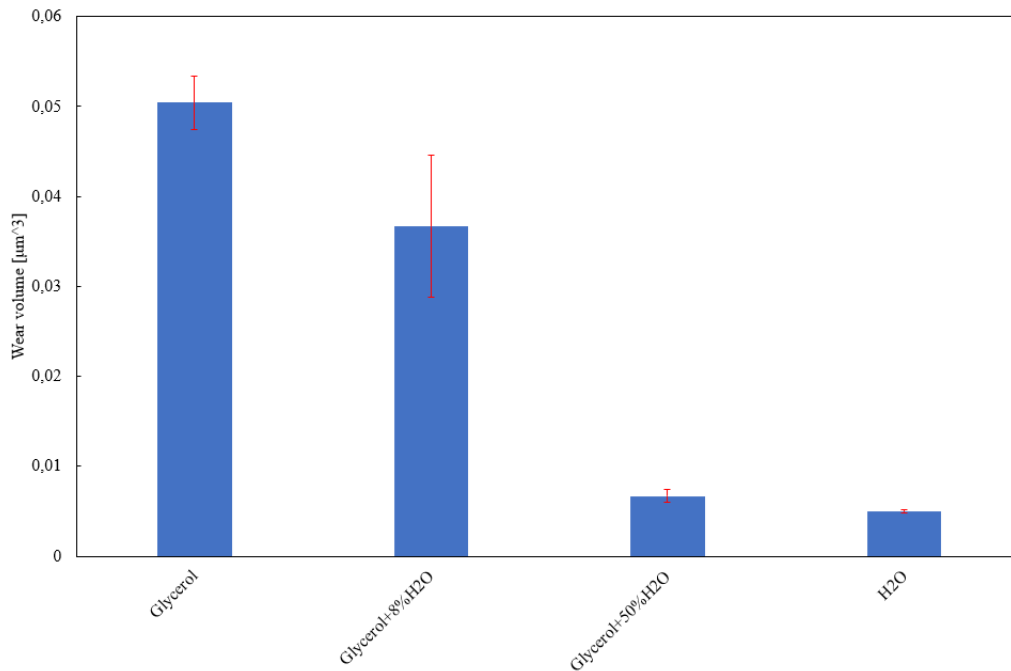


Figure 3.16: Wear volumes [ $\mu\text{m}^3$ ] of the worn surfaces (SS 316) lubricated with glycerol, glycerol + 8% H<sub>2</sub>O, glycerol + 50% H<sub>2</sub>O, and H<sub>2</sub>O.

Figure 3.17 shows the wear volumes from the tests lubricated with glycerol aqueous solutions with different additives. Glycerol + 8% H<sub>2</sub>O + 0.1% C12 had a wear volume of 0.033  $\mu\text{m}^3$ , and glycerol + 50% H<sub>2</sub>O + 0.1% C12 had 0.005  $\mu\text{m}^3$ . Glycerol + 8% H<sub>2</sub>O + 0.3% C12 had a wear volume of 0.036  $\mu\text{m}^3$ . Glycerol + 8% H<sub>2</sub>O + 0.1% PP had a wear volume of 0.022  $\mu\text{m}^3$ , and glycerol + 8% H<sub>2</sub>O + 0.1% PC had a wear volume of 0.034  $\mu\text{m}^3$ . Thus, PP had the lowest wear volume out of the additives in glycerol + 8% H<sub>2</sub>O. However, the 0.1% C12 in 50/50 glycerol/water solution showed the lowest wear volume out of all the additives in glycerol.

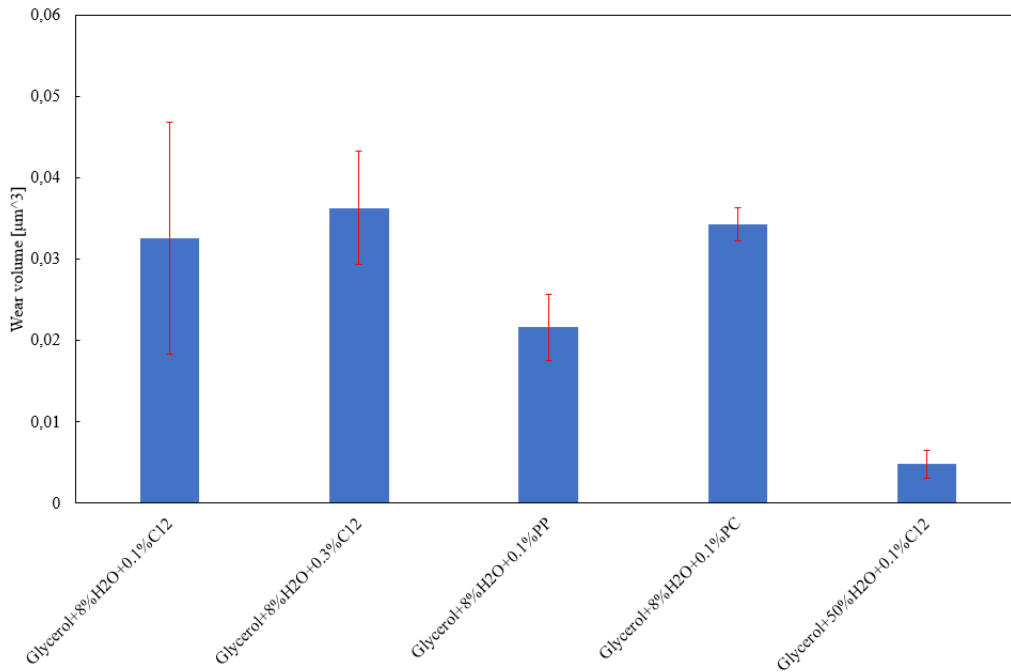


Figure 3.17: Wear volumes [ $\mu\text{m}^3$ ] of the worn surfaces (SS 316) lubricated with glycerol + 0.1% PP, glycerol + 0.1% PC, glycerol + 8% H<sub>2</sub>O + 0.1% C12, glycerol + 8% H<sub>2</sub>O + 0.3% C12, and glycerol + 50% H<sub>2</sub>O + 0.1% C12.

### 3.4.2 In PAO

The wear volumes from the tests lubricated with EAL 1, PAO + 1.0% ADTC or BL1232EL are presented in figure 3.18. EAL 1 had the lowest wear volume of  $0.009 \mu\text{m}^3$ . PAO with ADTC had a wear volume of  $0.013 \mu\text{m}^3$ , and PAO with BL1232EL had  $0.014 \mu\text{m}^3$ .

Figure 3.19 shows the wear volumes of the tests lubricated with pure PAO or PAO with 0.1% of additive PP, PC, or C12. PAO + C12 had a wear volume of  $0.012 \mu\text{m}^3$ , PAO + PP had  $0.010 \mu\text{m}^3$ , PAO + PC had  $0.013 \mu\text{m}^3$ , and PAO without any additive had a wear volume of  $0.009 \mu\text{m}^3$ .



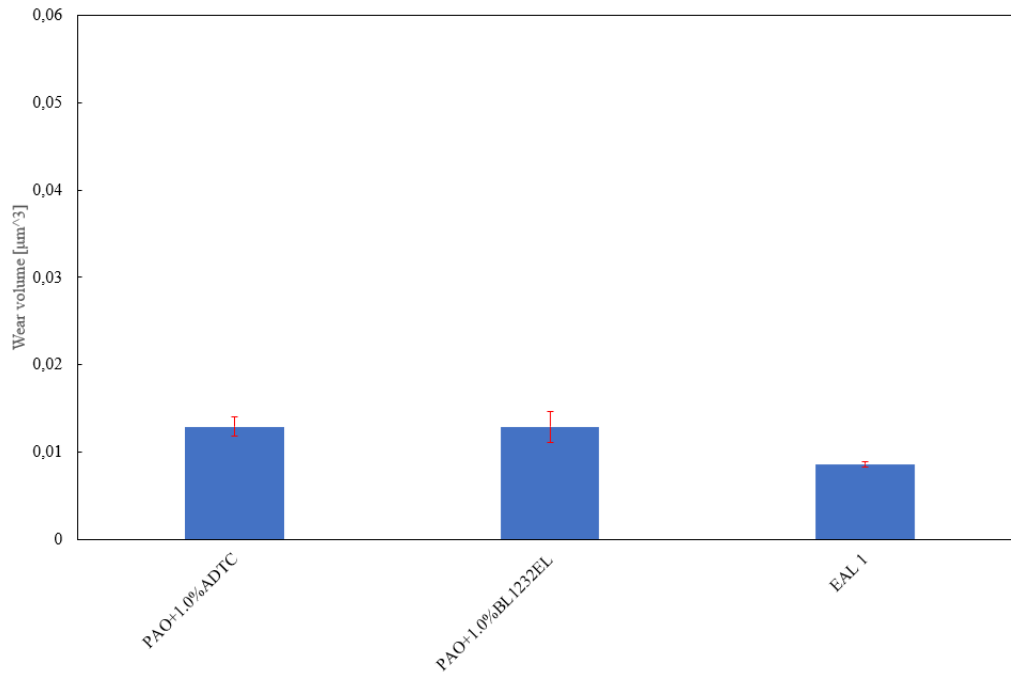


Figure 3.18: Wear volumes [ $\mu\text{m}^3$ ] of the worn surfaces (SS 316) lubricated with the reference lubricant EAL 1, PAO + 1.0% ADTC, or PAO + 1.0% BL1232EL.

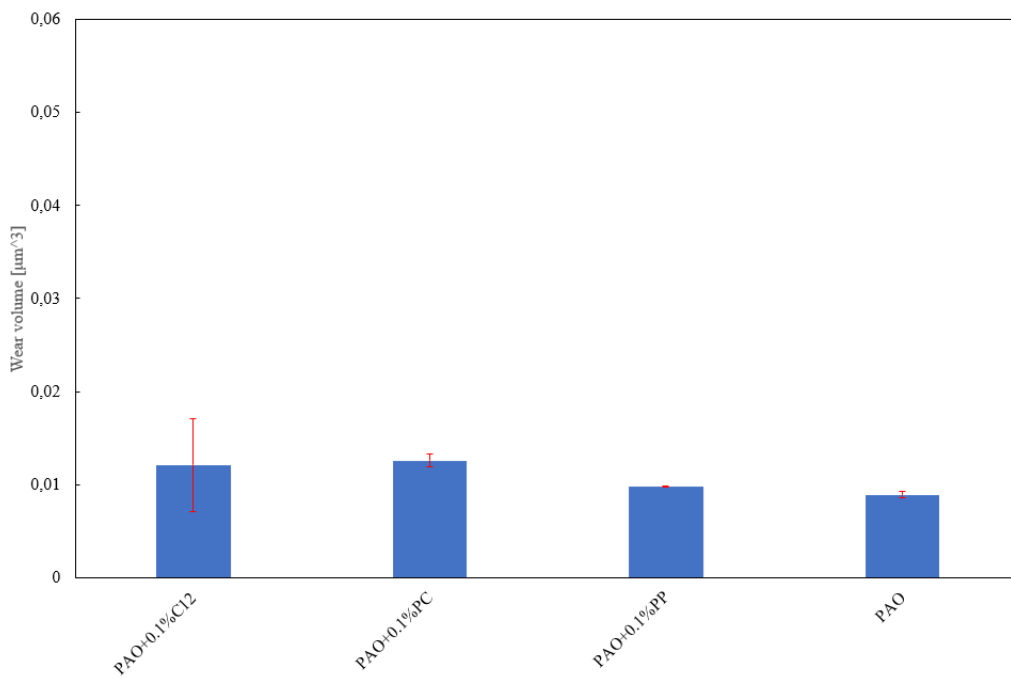


Figure 3.19: Wear volumes [ $\mu\text{m}^3$ ] of the worn surfaces (SS 316) lubricated with PAO, PAO + 0.1% C12, PAO + 0.1% PC, and PAO + 0.1% PP.

### 3.4.3 Images of the wear tracks

An IFM image of the wear track taken with 10X magnification is presented in figure 3.20. The surface was lubricated with glycerol + 0.1% PP, and the image shows how the wear track looks like in a 3D view. All the tested specimens had the same type of wear scar (only difference in volume) and therefore only one IFM 3D image is presented in this thesis. The color represent the differences in height and depth on the surface, and the wear track is clearly visible in the area with blue/turquoise color.

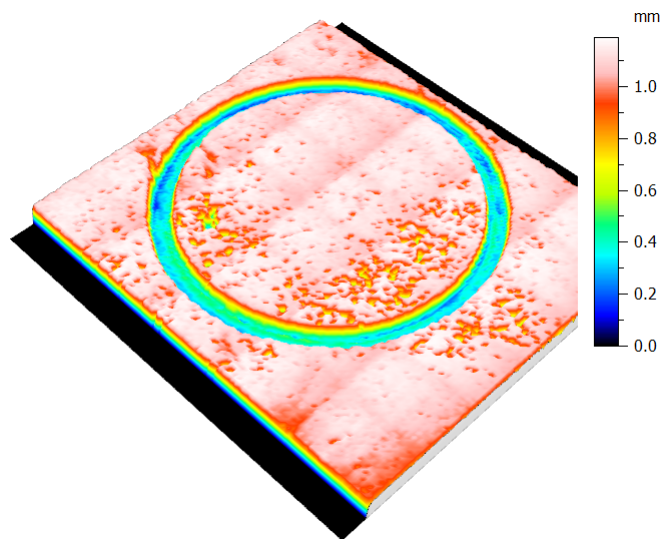


Figure 3.20: IFM image of the wear track of the SS 316 surface lubricated with glycerol + 0.1% PP.

After testing visual differences were observed in the wear tracks obtained. Figure 3.21 shows the wear track after testing of lubrication with (A) glycerol + 8% H<sub>2</sub>O + 0.1% C12 and (B) glycerol + 8% H<sub>2</sub>O + 0.3% C12 wear track after testing. In (B) there were observed a clear collection of wear debris (1) and colorless particles (2) on the surface. To be able to compare these surfaces with the reference lubricant EAL 1, an image of the EAL 1 wear track is shown in figure 3.22.

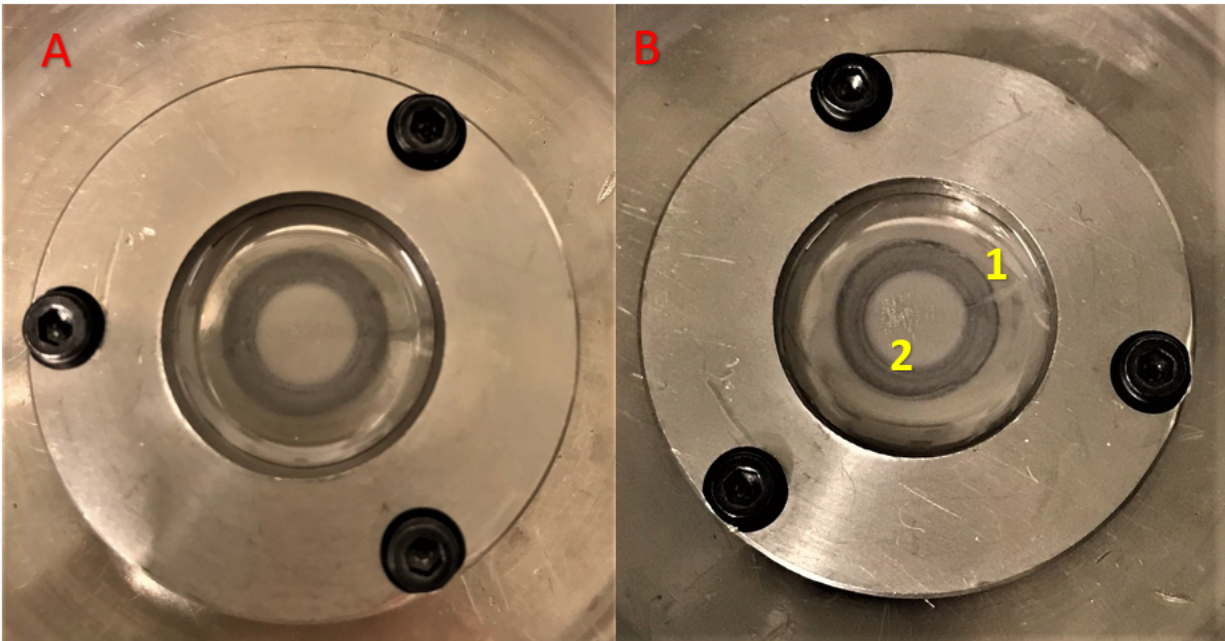


Figure 3.21: Images of the wear track after the pin on disk test for (A) glycerol + 8% H<sub>2</sub>O + 0.1% C12 and (B) glycerol + 8% H<sub>2</sub>O + 0.3% C12. (1) shows a collection of wear debris and (2) shows colorless particles in the middle of the wear track circle.

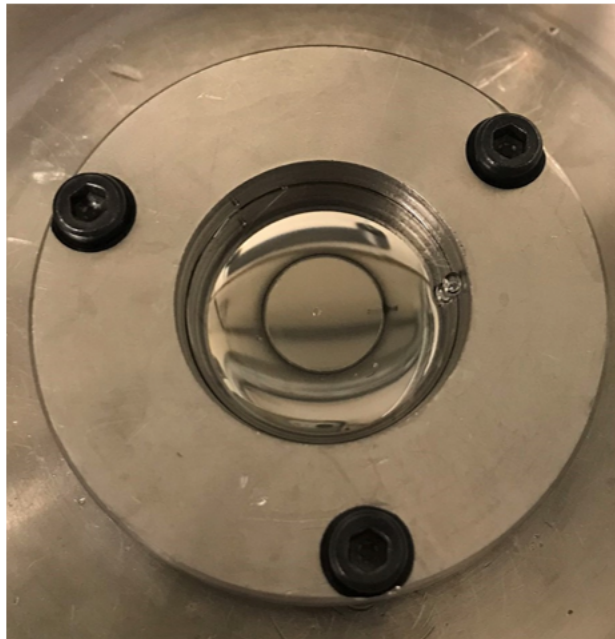


Figure 3.22: Image of wear track after pin on disk test lubricated with EAL 1.

The wear tracks were also investigated in SEM and with EDS. The results from the EDS could detect 0.21% P (error 20%) (presented in figure A.3 in Appendix), and hence, there was not performed any further EDS testing. SEM micrographs of the wear tracks of the surfaces lubricated with PAO, glycerol, and water are shown in figure 3.23. The figure shows more wear scars on the surfaces lubricated with glycerol and water compared with PAO. There are multiple black spots/areas on the worn surface lubricated with water, and some areas on the surface lubricated with glycerol. SS 316 surface lubricated with glycerol aqueous solution with C12, PC, and PP are shown figure 3.24. This figure shows the same type of wear scars as figure 3.23. In figure 3.25 it is shown SEM micrographs of SS 316 surfaces lubricated with PAO with C12, PC, and PP. Black areas are also seen on (b) and (c). EDS of these black spots indicates that these areas are lubricant residue or dirt.

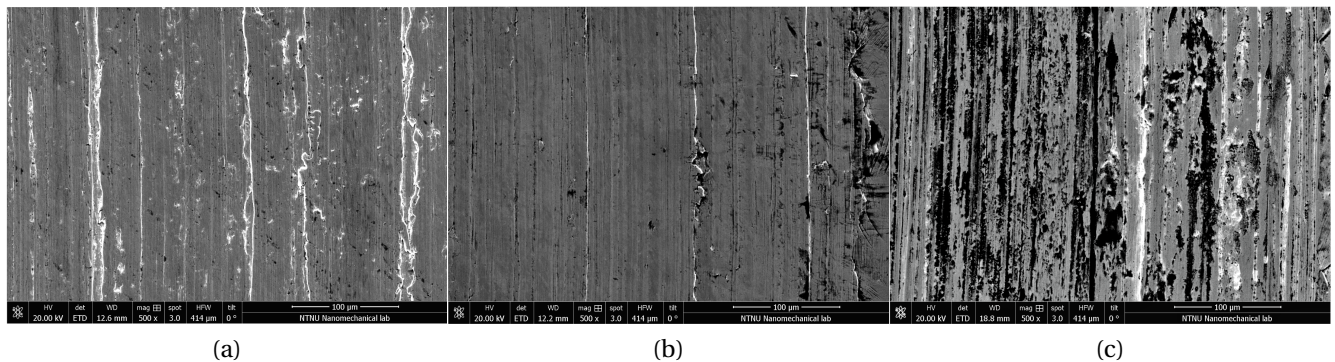


Figure 3.23: SEM micrographs of SS 316 surfaces after pin on disk tests lubricated with (a) glycerol (b) PAO (c) water.

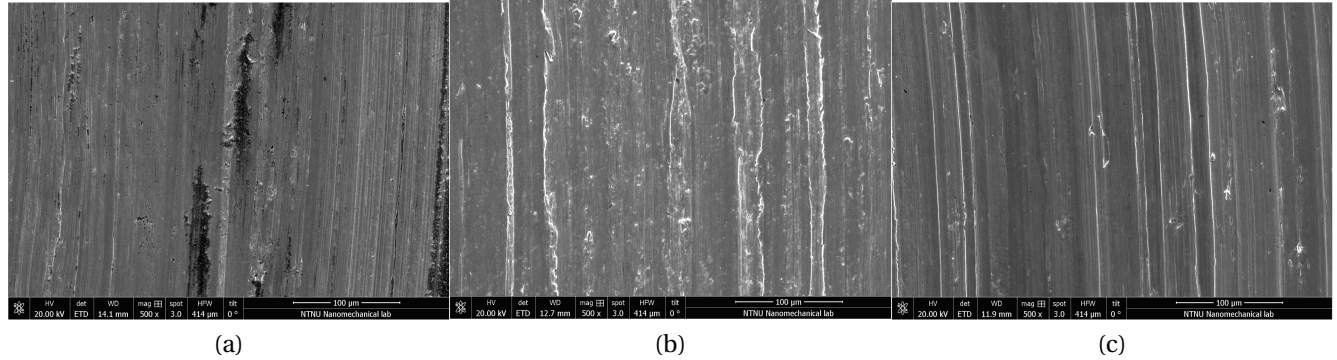


Figure 3.24: SEM micrographs of SS 316 surfaces after pin on disk tests lubricated with (a) glycerol + 8% H<sub>2</sub>O + 0.1% C12 + 0.8% amines (b) glycerol + 8% H<sub>2</sub>O + 0.1% PC (c) glycerol + 8% H<sub>2</sub>O + 0.1% PP.

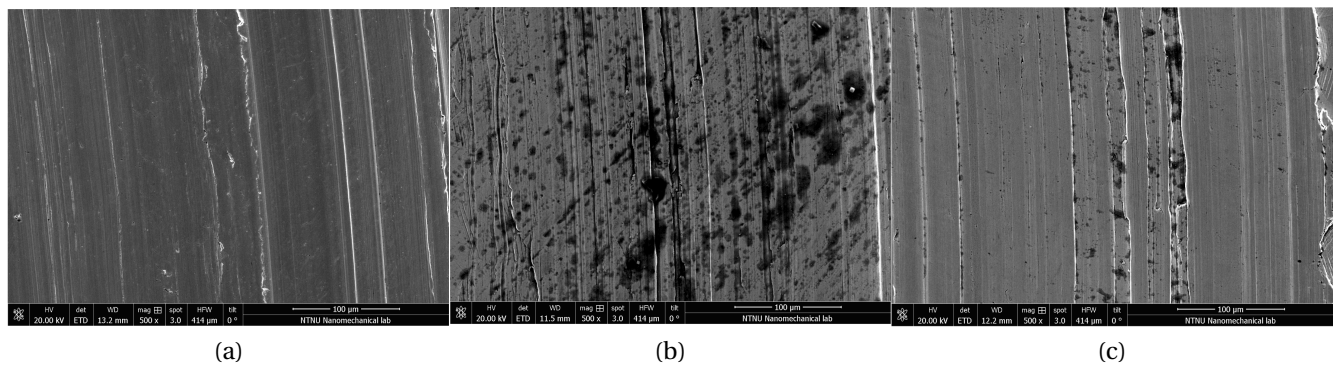


Figure 3.25: SEM micrographs of SS 316 surfaces after pin on disk tests lubricated with (a) PAO + 0.1% C12 (b) PAO + 0.1% PC (c) PAO + 0.1% PP.



# Chapter 4

## Discussion

A environmental acceptable lubricant need to consist of a base oil with the right eco-friendly characteristics. Since either glycerol or PAO are classified as EALs, the possibilities for these two were studied by several authors [17, 23, 28]. In this thesis PAO 10 was used, and according to literature low viscosity PAOs and PAO with short hydrocarbon chains fulfills the eco-labels requirements. Glycerol which is miscible with water, easy to dissolve, and a lubricant often used in the food industry is also a base oil that will fulfill the eco-labels requirements.

### 4.1 Rheological properties

In maritime gear components high viscosity fluids resulting in high film thicknesses are not wanted. Glycerol, which is a well known viscous fluid, will in these components need more energy to move the surfaces in contact compared to a commercially available EAL. In order to obtain the same rheological properties as the EALs it is necessary to decrease the viscosity of glycerol by addition of water. Shi et. al [16] found that by increasing the content of water up to 50%, the viscosity decreased about 200 times. In this master thesis lower amounts of water were used. However, it was a clear trend in the rheological study that the addition of water influenced the viscosity of glycerol, and that the viscosity decreased with addition of small amounts of water. Due to the fact that the wanted viscosity of the glycerol aqueous solution in this master thesis was approximately 68 mPas, the solution for further testing contained 8% of water. When comparing the rheological results of the three reference lubricants, EAL 1, EAL 2 and EAL 3,

adding 8% of water gave higher viscosity than all three reference lubricants (57 mPas compared with 43 mPas for EAL 1). Thus, some might consider to increase the water content to the highest amount tested in the present study (11%), however, it is still small amounts of water, and the difference between 9-11% of water did not follow a trend, since 11% of water had slightly higher viscosity than both 9 and 10%.

When it comes to the rheological properties of the two base oils used in the present study, it is clear that PAO behaves as a Newtonian fluid. Hence, the viscosity is constant with increasing shear rate. All tests were performed two times up to a shear rate of  $500 \text{ s}^{-1}$ , and a common trend for all the test was that the second run up to  $500 \text{ s}^{-1}$  showed a lower and more stable viscosity. A hypothesis can be that on the second run the molecules may already be in a more stable arrangement compared with the first run, which may lead to a more stable viscosity. On the other hand, it is well known that the viscosity is dependent on temperature, and the fact that the lubricant has been held at  $40^\circ\text{C}$  for a longer period of time in the second run can also be a reason for the small decrease of viscosity. According to Borrás et. al [17] and Zopler et. al [18], PAO can suffer from shear thinning at high shear rates. This was not a problem in the present studies, as the rheological studies were not performed at such high shear rates. For pure glycerol, the first run up to  $500 \text{ s}^{-1}$  behaved as a non-Newtonian fluid, as the viscosity decreased with increasing shear rate. On the other hand, the second run showed Newtonian behavior. Moreover, all the glycerol aqueous solutions showed Newtonian behavior independent of first or second run, which is in common with the results found by Shi et. al [16]. Therefore the non-Newtonian behavior of the first run of glycerol are a deviation from the literature.

The viscosity of the commercially available EALs showed all lower viscosity at  $40^\circ\text{C}$  in the rheological study than the reported values. This indicates that the test parameters or test equipment was different in this thesis than the reported values.

## **Conclusion**

Glycerol had the highest viscosity, but its viscosity can be reduced by adding water, which corresponds very well with the literature. The amount of water might be increased above the level of



8% that was used in this master thesis, as the viscosity of glycerol with 8% of water was slightly higher than the commercially available EALs. All lubricants showed Newtonian behavior, except the first run of pure glycerol. It was not observed any shear thinning behavior for either the PAO or the reference lubricants, however, high shear rates were not tested in the present studies.

## 4.2 Frictional performance

The base oil gives the lubricant most of its tribological properties and characteristics. In this master thesis it was used a polar (glycerol) and a non-polar (PAO) base oil. As already explained, water was added in the polar base oil to obtain a similar viscosity as the non-polar base oil. The tribological results showed that water had a higher CoF than both glycerol and PAO in boundary conditions, which means that water presents poor frictional performance. Water which has a low viscosity do not have the same properties to build a stable fluid film with high load carrying capacity between the surfaces in contact, leading to poor frictional properties. On the other hand, pure viscous glycerol did not have a higher CoF than the glycerol aqueous solution and PAO, indicating that low viscosity fluids affect the frictional performance more than viscous fluids. However, in the running in period where the contact between the asperities was high, water had relatively low CoF compared with the two other base oils. This indicates that water may build up a friction reducing film in the beginning of the test, but after a period of time this film breaks down and the CoF increases. Moreover, this performance can be correlated with the fact that both the base oils need time to react with the surface to create a film with some frictional reducing behavior. Both PAO and glycerol showed the same frictional performance without additives present, indicating that the polarity of the base oil does not influence the frictional performance in this case.

### 4.2.1 In glycerol

When it comes to the glycerol and the frictional performances of the additives, the solubility of additives plays a certain role. As mentioned, 8 wt% of water was used to obtain a glycerol solution with the same viscosity as all the other lubricants used in this research. According to literature [16] all polar compounds should be soluble in glycerol. C12 was used as an additive

to obtain good frictional performance, due to the possibility of formation of micelles and shear strength films. Observations done in this thesis point at the amount of water in the glycerol solution might be a decisive factor concerning solubility of C12. As explained by Bernat [34] the formation of micelles is possible in polar aqueous solutions if the amount of CA is kept below the CMC, and in this thesis the amounts used were below CMC. However, the frictional results showed that no micelles were formed with 8% of water because the CoF with the C12 solution was approximately the same as the glycerol without C12. On the other hand, the formation of micelles was clear in the solution with 50% of water, where the CoF decreased clearly. As mentioned, glycerol and water should have the same solubility performance, however the results showed that glycerol is depending on the amount of water added in the solution to obtain good solubility performance. As explained in the results the observation of particles in the wear track of the tests lubricated with C12 indicates that the C12 was not fully soluble with only 8% of water, and that the particles were separated during the tribological test period. The wear track was also sludgy compared with the wear track of the surface lubricated with EAL 1. According to literature [34] the solubility of CA in polar lubricants is depending on the length of the hydrocarbon chain, and due to the fact that glycerol is a viscous liquid compared with water the length of C12 chain can be too long to be soluble in glycerol and glycerol + 8% H<sub>2</sub>O. Hence, the hypothesis that the water film, which is generated in glycerol aqueous solution during the shearing of the lubricant in boundary condition, can play an important role when it comes to the solubility of the additives in the lubricant. It is possible that the additives get solved in this film in presence of free water molecules. However, the test with phenolphthalein did not indicate any different phases in the glycerol/water/C12/amine solutions, so this could not confirm the hypothesis about the water film. The test could only show that the pH (which also was measured) was higher in solutions with water. This may indicate that the water film only gets created when shearing of the lubricant is present.

According to literature, ILs can provide both reduction of friction and anti-wear performance. When it comes to the frictional performance of the ILs (PP and PC), did not show any effect on the CoF in solution with glycerol aqueous solution. The main difference between PP and PC is the cation group, where PC contains a carboxylate group and PP contains a cation with

phosphor. They both have an anion counting phosphor. Therefore, it might be that the ILs are not acting as friction modifiers in this case.

### 4.2.2 In Pao

In PAO there was no problem with the solubility of the additives tested in this master thesis. According to several studies [17, 22, 25, 26] this could be a problem due to the lack of polarity in PAO. However, it was observed different frictional performance of the additives. Concerning the frictional behavior in the running in period it was high for all solutions, except the reference lubricant, EAL 1, which had a low CoF in the running in. The reference lubricant was a fully formulated lubricant, which means that the lubricant probably contains additives which can react with the surface in the running in period where no stable boundary film is built up. Hence, comparing the reference lubricant with the lubricant with the ADTC/BL1232EL lubricants which also are categorized as fully formulated additive packages, the EAL 1 contains additives that performs better during all stages of the condition tested in this master thesis. It is difficult to establish the mode of action of the friction modifier in the commercially available reference lubricant and additive packages, as the chemical compositions are unavailable.

Concerning the effect of C12 in PAO, it was observed a decrease in the CoF which indicates that C12 acts as a friction modifier. The non-polar PAO has high solubility of the hydrocarbon chain in C12, which promotes formation of multilayers [45]. The formation of these multilayers gave the PAO with C12 the same frictional performance as EAL 1 in the steady state region. Rudnick [47] explain that C12 promotes formation of adsorbed layers. In these layers the hydrocarbon chain will be soluble in PAO and the polar head of the C12 molecule will get attached to the metal surface. It is therefore a reason to assume that the multilayers described by Bernat and the adsorbed layers are the same type of layers, and that these lead to a reduction in CoF in boundary conditions. Comparing the behavior of C12 with EAL 1, an assumption can be made that EAL 1 also contains FM from the same mode of action as the one C12 is a part of.

The ILs, PP and PC, obtain different frictional performances in PAO. Both PP and PC have some frictional effect in PAO, however the performances of both are less than the frictional perfor-

mance of C12. PP shows lower CoF than PC, and it is therefore a reason to believe that it is the different anion in the ILs which has an affects the frictional behavior.

## **Conclusion**

In this master thesis one polar (glycerol) and one non-polar (PAO) base oil have been formulated with addition of four different types of additives. The tribological tests of the polar and the non-polar base oils shows similar frictional performances without addition of additives, and both PAO and glycerol show lower CoF than water. Overall, the best frictional performance was reached with PAO + 0.1% C12. Hence, C12 behaves as a friction modifier due to formation of adsorbed layers on the surface in boundary conditions. Concerning the ILs, both PP and PC did not result in any positive frictional performance in glycerol aqueous solutions. However, in PAO PP acts as a friction modifier by reducing the CoF. This leads to different behavior of PP in PAO and glycerol. PC did not act as a friction modifier in either of the base oils.

## **4.3 Wear**

According to Torbacke [2] different wear mechanisms can be expected in a tribological contact. Also tribochemical wear can be present by chemical reaction between the lubricant and the surface. The investigation of the wear tracks showed that all wear scars are independent of the lubrication used, and they have suffered from the same wear mechanisms. As mentioned in the results, no tribofilm on the surface was clearly detected. However, this is probably because the tribofilm has been washed off during the cleaning procedure with acetone.

### **4.3.1 In glycerol**

The results showed that pure water gave the best wear performance and had the lowest wear loss out of all tests performed. Glycerol aqueous solutions also showed a clear trend that increased water content lead to a lower wear rate compared to pure glycerol, and vice versa in comparison with water. In this master thesis SS316 was used, and it is therefore important to take the electrochemical response of the stainless steel in different fluids into account as discussed by Bernat [34]. During the tribological testing the passive film on the steel surface will be removed, which

creates a galvanic coupling where the wear track (anode) is exposed to the electrical conductive lubricant, and the un-worn surface will act as a cathode. This will increase the chance for tribocorrosion on the metal surface, leading to increased wear rate. Bernat has explained that some spices (glycols in his case) showed faster cathodic kinetics than pure water which lead to increased wear. No polarization testing was performed in this master thesis to confirm this phenomenon with glycerol. However, it may explain why glycerol/water solutions show higher wear loss than pure water in this case. It is also important to take into account that the water used in this thesis was distilled water, so the water is not as reactive due to low amount of ions and other species. Comparing the results found in this master thesis with the results from Shi et al. [16] there is different behavior on the wear loss with increasing water content. Shi experienced increased wear loss with increasing water content in glycerol solutions. In this master thesis, the opposite trend was observed. Another interesting observation was the high wear loss in pure glycerol as lubricant. In the present studies, glycerol showed poor anti-wear properties, and one hypothesis can be that glycerol reacts chemically with the surface, leading to increased wear loss. However, the methods used in this master thesis did not detect the chemical reactions which occurred during the testing. So, it is not known which influence glycerol may have, and how it reacts with the metal surface. Neither there is literature found on this topic, which might shed some light on which mechanisms to be involved.

Concerning the effect of the additives on the anti-wear it has been suggested that tribocorrosion occurs due to the water present in the solution. However, the results from the IL, PP, performs best out of all additives in the 8% of water solutions. This indicates that PP, which did not have any frictional effect, behaves better as an AW additive. Another interesting observation was the effect of the amount of C12 in the 8% water solution. With 0.3% C12 the wear increased by a factor of 2 compared to 0.1% C12. This underlines the fact that increased amount of C12 increases the chances of tribocorrosion on the worn surface, as described in the section above when water is present. However, in the solution with 50% water the wear decreased compared with the 8% of water solution. A reason for that can be that the amount of additives that can react with the surface, and the effect of tribocorrosion was too low to overrun the effect of water.

### 4.3.2 In PAO

PAO showed excellent wear properties, indicating that PAO did not increase the chance for tribochemical wear. A clear trend in PAO showed that pure PAO obtained better wear properties than the mixed solutions. This indicates that the additives reacted chemically with the surface, as FMs do, which may increase the wear loss of the worn surface. Comparing the additive solutions with both the additive packages and EAL 1, EAL 1 showed best AW performance, implying that they have used different environmentally acceptable AW additives in the commercially available lubricant.

The additives used in the present study had very little different influence on the wear rate. PAO + PP had the best anti-wear properties out of the all the tested additives and additive packages in PAO. This means that the chances of formation of protective layers on the surface is present when PP is the additive. However, the wear performance of pure PAO is still better without addition of additives. Thus, PAO may not need the addition of AW additives to obtain good wear properties.

### Conclusion

Glycerol and glycerol aqueous solutions showed all an increased wear rate compared with the PAO solutions. This indicates that glycerol reacts differently with the steel surface than PAO. Water present in glycerol might increase the chances for tribocorrosion of the worn steel surface, however pure glycerol leads to more severe wear. Concerning additives, none of them showed clear AW properties. PP and C12 both showed less wear loss in both PAO and glycerol aqueous solution (C12 in solution with 50% water). However, it is important to keep in mind that it is difficult to separate FM and AW additives in boundary conditions as explained by Rudnick [7]. The interesting observation was that water was the solution which gave lowest wear volume out of all the lubrication solutions tested in this thesis.

## 4.4 Comparison of the effect of additives

Finding a combination of base oils, additives, and the right amount of the additives is a challenging task. An interesting observation was the different tribological behavior of PAO and glycerol. The CoF was not affected by the polarity of the base oil, however, the wear was largely influenced. This indicates that the polarity of the base oil can influence how the base oil reacts with the surface. In this case the polar base oil, glycerol, influenced negatively, which led to increased wear rate. According to Cen et. al [20], polar lubricants produce thinner protective reaction layers, leading to higher wear rates, explaining why glycerol showed higher wear rates compared to PAO. Since polar lubricants have higher affinity to the metal surface than non-polar lubricants, will the additives in polar lubricants have less surface space to use as reaction sites compared to the non-polar lubricants.

It is difficult to establish the different behaviors of friction modifiers and anti-wear additives in boundary conditions since they are adsorbed on the same sites on the surface. Taking this into account it is clear that C12 had better frictional performance both in PAO and in glycerol than the ionic liquids tested in this master thesis. In glycerol the water content must be high enough to establish the formation of micelles to obtain good frictional performance. On the other hand, that will affect the viscosity of the lubricant and it is important to keep the CMC in mind both when it comes to micelles formation and that the wear cannot be improved when the amount of C12 is below the CMC. The hydrocarbon chain in C12 can also be too short to obtain any good anti-wear performance, which has been reported by studies comparing the C12 solution with the base lubricant [34]. Considering the present rheological results, a higher amount of water mixed with glycerol might have improved both the solubility and the wear resistance. It may also be mentioned that the solubility of additives in glycerol is not a widely researched topic, and it is therefore difficult to establish a clear theory on what is happening without further testing.

In glycerol the IL, PP, did not show any frictional performance, though in PAO the PP had some frictional performance. Considering the AW performance, PP showed decreased wear rate in both glycerol and PAO. This indicates that the frictional part of the ionic liquid molecule did

not perform as good in polar lubricants as in non-polar lubricants. The reason for this can be that the solubility of the molecule is depending on the polarity of the base oil. When it comes to evaluating the effect of PC, it did not have any effect in both PAO and glycerol. Probably, too little amount of additive was used to obtain any visual effect under the tribological conditions used in this master thesis.

One task of this master thesis was to find a formulation that might be able to absorb more water than the reference lubricants. It is well known that glycerol changes viscosity in contact with water, and as already discussed, the chance for tribocorrosion increases. However, neither glycerol nor PAO does hydrolyze in contact with water, and because of that they perform better than the synthetic ester based reference lubricants.



# Chapter 5

## Conclusion

The goal of this master thesis was to formulate an environmentally acceptable lubricant for use in maritime gear components. This was done by performing a rheological and a tribological study on one polar (glycerol) and one non-polar (PAO) base oil. It was tested four environmentally acceptable additives, one carboxylic acid and three types of ionic liquids compared with commercially available lubricants. By the results obtained in this master thesis the following conclusion can be made:

- The literature review showed that both glycerol and PAO are potential base oils for environmentally acceptable lubrication.
- Glycerol had problems with the solubility of the additives, which led to glycerol failing to exploit the properties of the additives.
- PAO with the carboxylic acid (C12) showed improved tribological performance in boundary condition.
- Glycerol showed higher wear rate than PAO, indicating that the wear rate was influenced by the polarity of the lubricants.
- Water could reduce the viscosity of pure glycerol to obtain better rheological properties, but this can increase the chance for tribocorrosion, implying increased wear rate on the worn surface.

From this it can be concluded that PAO with C12 had the best frictional and wear performance out of all the tested lubricants in this master thesis. This means that PAO could be a good choice for base oil when formulating an environmentally acceptable lubricant.

# Chapter 6

## Further work

This master thesis addressed the formulating and testing of a new environmentally acceptable lubricant for gear components with use of one polar base oil and one non-polar base oil. Emphasis was placed on different types of friction modifiers and anti-wear additives, kept in mind that a fully formulated EAL must consist of other types of additives to obtain excellent lubricating properties. However, there are still central topics that should be further investigated. These topics are:

- Since this master thesis experienced increased wear loss when glycerol was used as a lubricant, it would be interesting to explore why this is happening. This can be done by investigating how the glycerol reacts with the metal surface. Is it the polarity of glycerol which is affecting this, or are there other reactions involved. It will also be interesting to study the tribofilm on the steel surface. The present thesis also uncovered difficulty with solubility of additives in glycerol. Further investigation should explore factors influencing the solubility.
- Establish a fully formulated environmentally acceptable lubricant for maritime gear components with all necessary additives, FM, AW, corrosion inhibitors, and antioxidants. The EAL can also be based on other base oils than the ones which were used in this thesis. However, since low viscosity PAOs can be EAL approved, this would be a good choice to use in further testing.



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# **Appendix A**

## **CoF, wear, and EDS results**

### A.1 CoF and wear

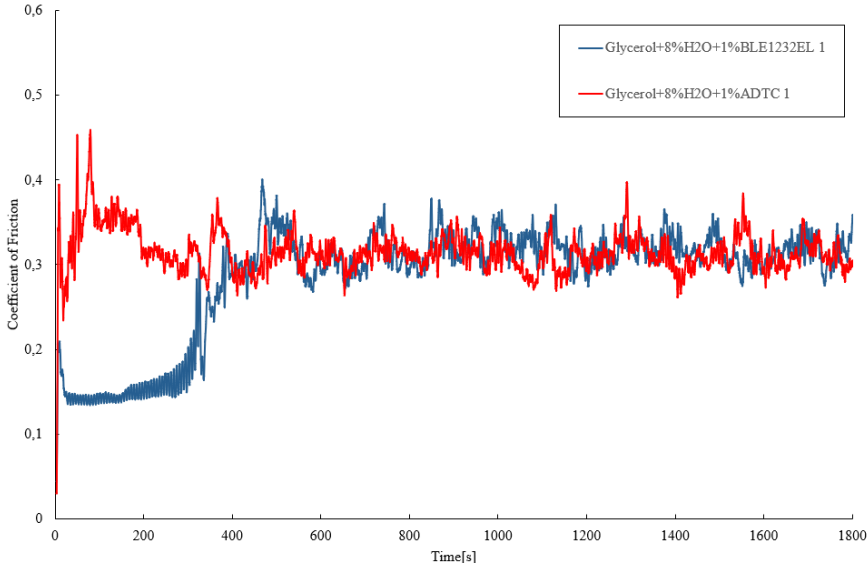


Figure A.1: Frictional performances of glycerol aqueous solutions with 1.0% of ATDC or BL1232EL.

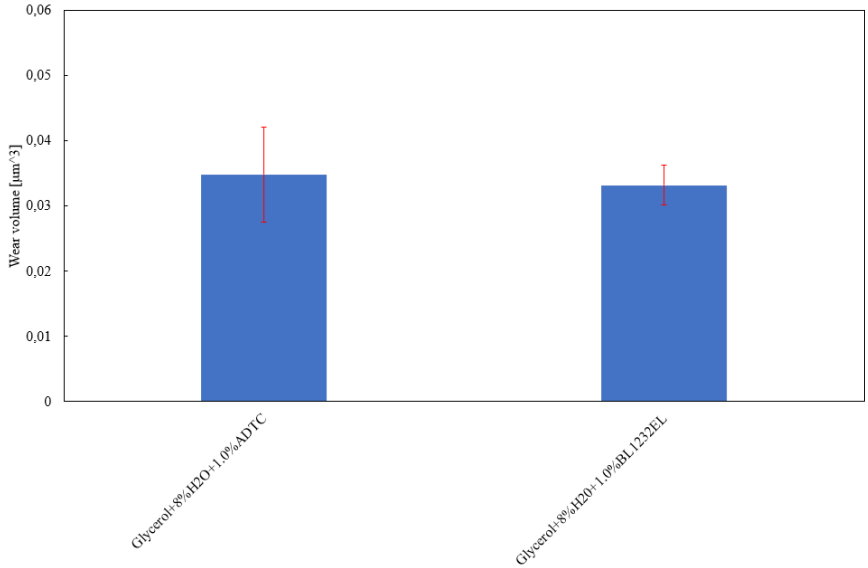


Figure A.2: Wear loss of glycerol aqueous solutions with 1.0% of ATDC or BL1232EL.

## A.2 EDS

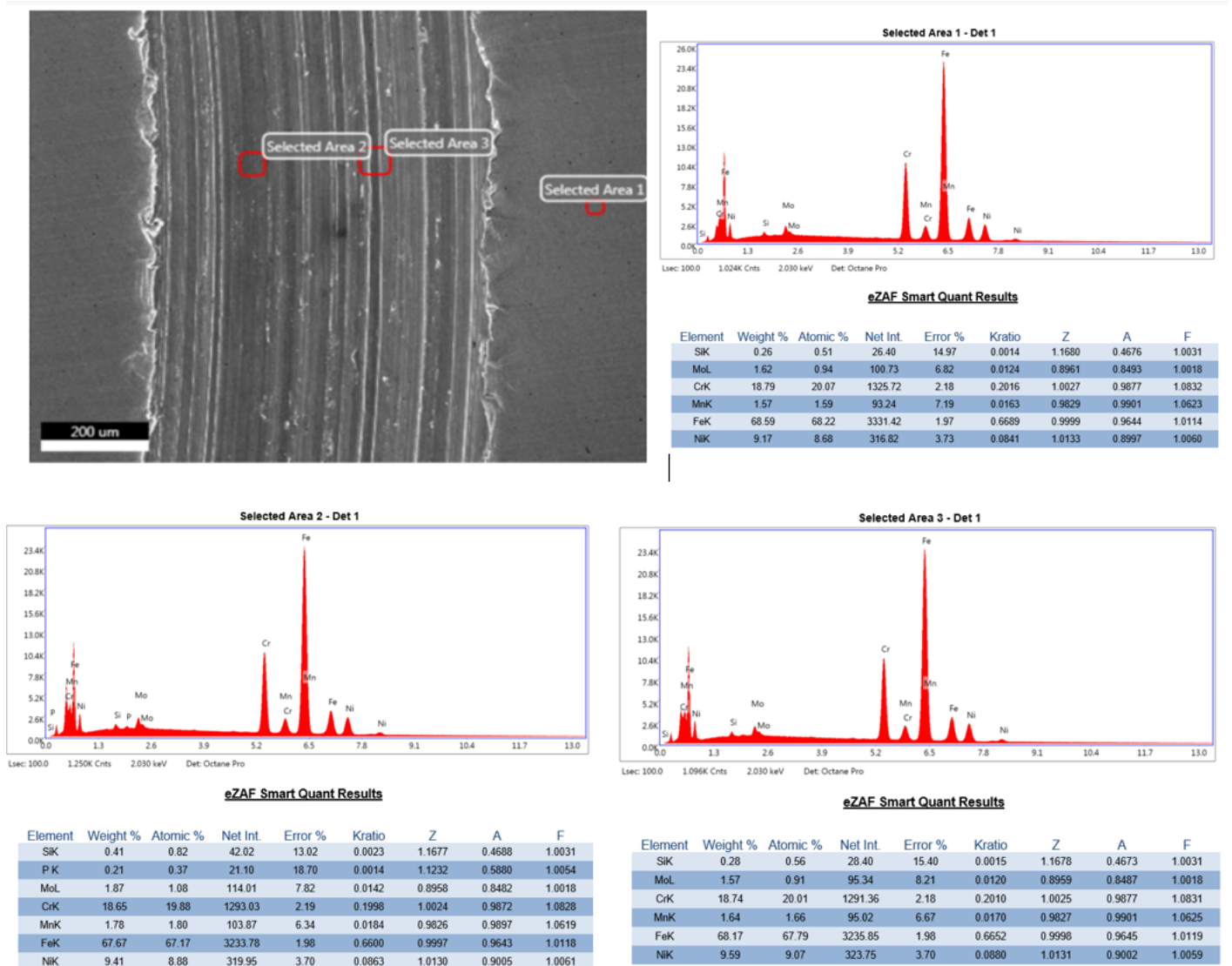


Figure A.3: SEM image with EDS scan of SS316. The test was lubricated with glycerol + 0.1% PP.

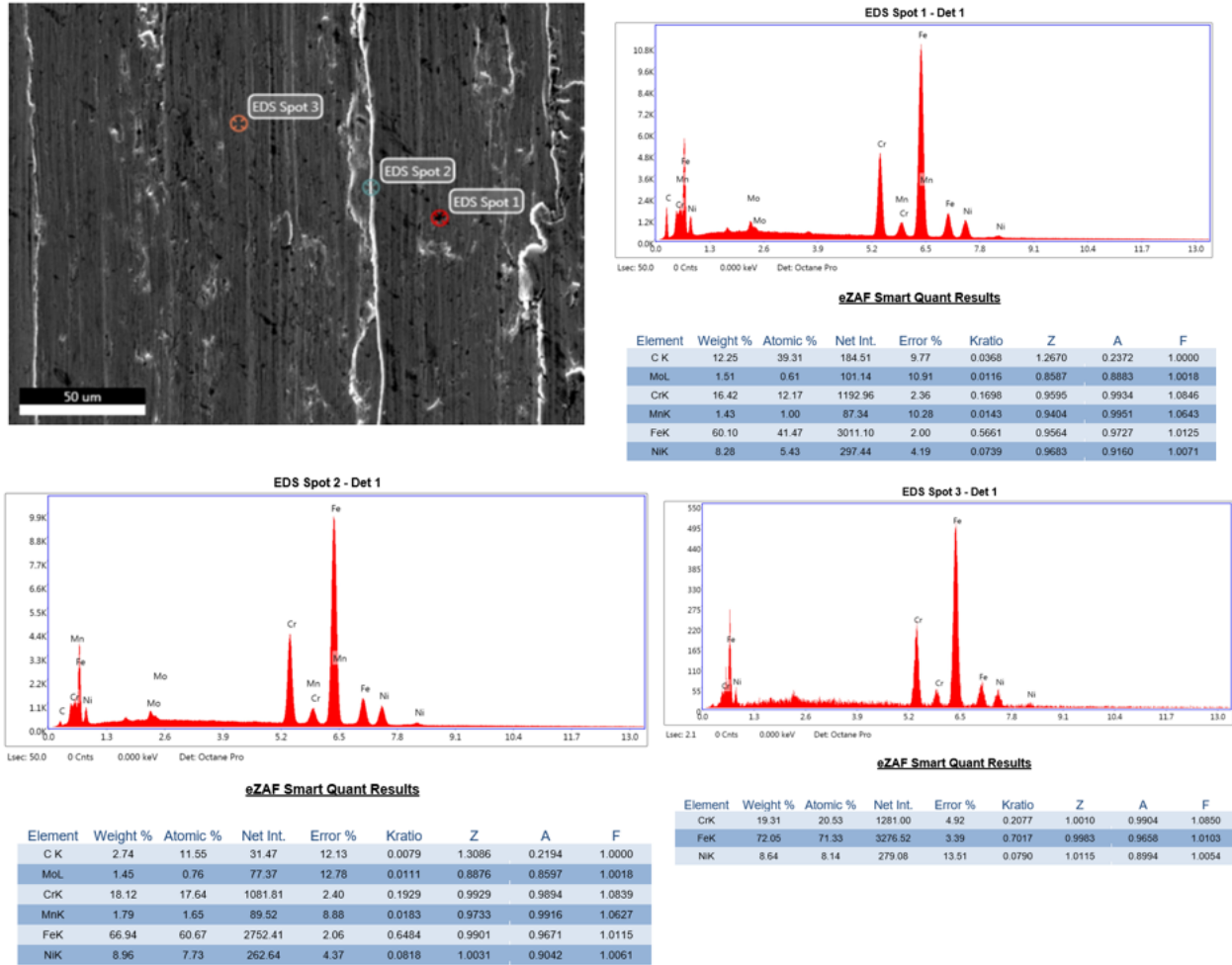


Figure A.4: SEM image with EDS scan of SS316 lubricated with glycerol.