INDUSTRIAL BIO-LUBRICANTS PERFORMANCE AND CHARACTERIZATION

by

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Abstract

The general trend towards the use of high performance lubricants and environmentally friendly products supports the design of new industrial lubricants. Therefore, there are good practical reasons to extend the research related to lubrication. Bio-oils, as promising growing substitutes for mineral oils, need more research to deal with new and inherited problems. Meanwhile, there is no complete understanding of the lubrication phenomenon, nor a complete rheological characterization of oil lubricants. This research is an effort to study industrial bio-ubricants and to develop a more comprehensive approach, at the same time correlating their rheological and tribological behavior.

Different commercial canola oil based lubricants were studied using different techniques. For validation and comparison, engine oil, silicone oil and mineral hydraulic oil were tested. Bio-lubricants exhibited constant viscosity at both moderate and high shear rates and shear thinning at low shear rates and temperatures below 30 degrees Celsius. Frequency sweep tests revealed a significant viscoelasticity of bio-lubricant which developed over time.

Time dependence, structure recovery, gap size effect, surfactant behavior, and geometry's material influence were all investigated. A high pressure cell and a polarized light microscope coupled with the rheometer were used to investigate the bio-lubricants.

Thermal analysis was conducted using a differential scanning calorimeter. Several transition points were identified in the range of temperatures from -30 to 100 degrees Celsius, and the results have been connected to the viscoelastic behavior.

Different tribological tests were used to investigate the lubricity of lubricants and biolubricants added by liquid crystals. The coefficient of friction, at tested temperatures, and the wear rate were observed over time. Adding two percent of ionic liquid crystals improved the wear resistance of the oil, but the bio-lubricant had the lowest coefficient of friction. This research could be considered as pioneer work. An attempt was made to achieve profound perspective matching between rheometry, tribology and thermal analysis. Some assumptions explaining the rheological and tribological behavior were hypothesized and associated with arguments and discussions. Based on, Imaginary scenario of bio-hydraulic oil behavior within a small gap was visualized.

Preface

This thesis was written by Abdul-Hamid Elemsimit under the supervision and guidance of Dr. Dana Grecov, who provided the topics for this research: the rheological characterization of bio-lubricants; the tribological performance of bio-lubricants; the rheological and tribological impacts of liquid crystal additives on bio-lubricants; and the thermal analysis of bio-lubricants.

All the rheometery experiments were conducted in the Polymer Rheology lab at the University of British Columbia. The author both designed and performed the experiments, as well as prepared the used solutions.

Dr. Louise Creagh, of the University of British Columbia, facilitated and instructed using the Bio Thermodynamics lab, where the TA experiments were done. The author designed the experiments, prepared the samples, and performed the experiments.

For the four ball tests, conducted by the National Research Council (NRC), Vancouver, the author provided the experiment conditions based on international standards, and examined the scars in the Electron Microscope Laboratory, University of British Columbia, under the supervision of a specialist technician. In a related work, the author prepared the samples, decided the testing conditions, and conducted the experiments of pin-on-disk in the Pulp and Paper Centre, at the University of British Columbia (UBC).

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List of Symbols

C_p	heat capacity
f	friction force
G^{\prime}	storage modulus
$G^{\prime\prime}$	loss modulus
G^*	complex mudlus
h	gap size
h_m	measured gap
М	measured torque
Ν	normal force
p	contact presure
p_o	presure in the center of the contact area
Q	heat
R	the radius of the geometry
r_o	the radius of contacting area
SS_{Cs}	steady state measurement in controlled stress

SS_{Cr}	steady state measurement in controlled rate mode
t	time
t_i	integration time
t_s	sample time
Ω	angular velocity
eta	heating rate
γ_A	shear amplitude
γ^o	shear rate
γ^o_R	maximum shear rate at the rim of the Parallel plate geometry
γ^{o}	shear rate tensor
δ	phase angle
ε_g	gap error
ε_{f}	error in measured friction force
η	shear viscosity
η_o	zero shear viscosity
η_m	measured viscosity
λ	relaxation time
μ	Coefficient of Friction
σ	shear stress

- σ_R^o maximum shear stress at the rim of the Parallel plate geometry
- $\bar{\bar{\tau}}$ stress tensor
- $\omega \qquad \qquad \text{angular frequency} \qquad \qquad$

List of Abbreviations

ASTM	American Society for Testing and Materials
CFD	Computational Fluid Dynamics
DSC	Differential Scanning Calorimetry
ILC	Ionic Liquid Crystals
ISO	International Standards Organization
LC	Liquid Crystals
LC50	Lethal Concentration test
LD50	Lethal Dose test
LVDT	Linear Variable Differential Transformer
NRC	the National Research Council
SAM	Self Assembled Monolayer
SAOS	Short Amplitude Oscillation Shear
ТА	Thermal Analysis
UBC	University of British Columbia
VI	Viscosity Index

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who believes in knowledge and appreciates the education as nobody does; who has never imposed any axioms on my thoughts or asked me to stop asking why; and he was the stronger motivator to be in this position.

Chapter 1

Introduction

1.1 Overview

The general trend towards the use of high performance lubricants and environmentally friendly products supports the design of new industrial lubricants. Therefore, there are good practical reasons to extend the research related to lubrication. Bio-oils, as promising growing substitutes for mineral oils, need more research to deal with new and inherited problems. In terms of the tested material and similar studies, this research could be considered as pioneer work.

1.2 Motivations

Considerable applications for the subject of this study are worth the research on this area, economically. The world market for lubricants will be presented in this chapter, while the following is a list of economic motivations:

- Lubricants have a large growing market.
- Implementing lubricating technologies will lead to more efficient systems.
- There is a renewable demand for special purpose lubricants; among them are biodegradable lubricants

Besides, there are more motivations to use bio-lubricants specifically:

- Bio-oils come from sustainable resources
- They have advantage over mineral oil regarding environmental and health risks
- Legislations are putting more restrictions on polluting technology
- Using bio-oils decreases the liability insurance costs that come with using or producing harmful materials [1]
- Using bio-oils decreases disposable costs [1]
- Bio-oils have a high viscosity index, and very good lubricity.
- Improving a company's public image
- It diversifies the uses of rapeseeds

All of the mentioned advantages of using bio-oils as lubricants do not come without a price. There is not enough supply from vegetable oils to subtitute the mineral oils nowadays. Furthermore, they have poor oxidation resistance. Regardless of the economic motivations, there are number of academic motivations that encourage research on lubricants generally and bio-lubricants specifically:

- The rheological characterization studies on oil lubricants are still limited.
- There is still a gap between real cases and mathematical models.
- There has been no mathematical model developed specifically for lubricants.
- The lubricating phenomenon is not yet fully understood.
- There is a gap between micro & macroscopic, and rheological & tribological studies
- Not all the studies on mineral oils can be generalized to bio-oils; they differ in many aspects.

• Continuing innovation

While constitutive equations fail to represent the real case of viscoelastic lubrication, quantitatively, the experimental studies are inadequate. Experimental work on lubricants is challenging. The extreme conditions, such as the very high shear rate, very high pressure, and very narrow gap, needed to make the measurements can make it very difficult. Where clearance of 50 microns is a large distance in lubrication, the usual gap in a rotary rheometer varies from 0.5 to 1 mm. Nonetheless, the nano-technologies, such as electron microscopy, atomic force microscopy, and x rays, have managed to reach new levels of research, especially understanding the Self-Assembled Monolayer (SAM). However, it is not easy to use these technologies under harsh conditions. In spite of a general trend to welcome every sustainable and environmentally safe technology, the competitive quality of bio-lubricants still needs to be proven, as they are yet an unfamiliar product to consumers. Bio-oils also have completely different chemical compositions from mineral oils. This means that not all of the improving additive packages that worked well with mineral oils are compatible with bio-oils.

1.3 Objectives

Figure (1.1) illustrates the idea behind this research. The ultimate goal is formulating a more credible model based on experimental work done specifically on lubricants. The new model should approach the real case more exactly. It should show a match among the different views, such as: rheology, tribology, and microscopy. The aimed model should fill the present gaps and answer some raised questions.

Accordingly, the objectives of the present research are listed as follows:

- To characterize bio-lubricants Rheologically
- To evaluate the tribological performance of bio-lubricants



Figure 1.1: Research goal

- To investigate the compatibility of liquid crystals additives with bio-lubricants
- Understanding the boundaries and hydrodynamic lubrication mechanisms in biolubrication

1.4 Scope

This work is an attempt to achieve the drawn goal using available resources. Figure (1.2) shows the plan of this work.

Later in this chapter, some introductory surveys about the lubricants market and canola oil were presented. Further, some physical background about related topics were explained briefly. The Literature Review was included in the second chapter, the methodology. The rest of that chapter was devoted to the rheometery methods. For the purpose of sequentiality, the descriptions of the tribological and thermal analyses experiments will be postponed to chapters 4 and 5. The research tools were classified into two types of tools: experimental and theoretical. The main tool in this research was the rotary rheometer. The rheometrical experiments are described in chapter 3.



Figure 1.2: Research plan

The controlled experimental conditions included shear, temperature, geometry materials, pressure, and surrounding medium. As well, the lubricants were examined under a polarized light microscope. After the behavior of the interesting oils became more recognizable, a differential scanning calorimeter (DSC) was used to support the assumptions we had begun to build. Chapter 4 is where the thermal analysis work was presented. The lubricity of the bio-lubricant was the ultimate goal therefore the tribological performances of bio-hydraulic oil and liquid crystal additives were presented in Chapter 5. Because all the right paths should end in one destination, we tried to connect the results in the last three chapters as much as possible. In the last chapter (Chapter 6), the conclusion and future work were presented. Even though the assumptions built were based on consistent experimental results and supported by the literature, we cannot call it confirmed. Thus, we organized the conclusions in the form of hypothesises and arguments.

1.5 The Lubricants Industry

Despite the fact that friction is one of the forces that keeps the various elements of the universe attached to each other, tremendous effort is exerted to reduce and overcome this natural friction, in order to move things with less energy. Where half the consumption energy is dissipated as friction [2], another researcher estimated that the energy lost due to friction could be saved, based on present technologies, with about 0.4% of the gross domestic product in Western industrialized countries [3]. On the other hand, lubrication is one of the oldest and most widely used techniques employed to reduce friction. According to a World Lubricants report from the Freedonia Group [4, 5][4, 5], the global demand on lubricants will reach 40.5 MT in 2012, with an increasing rate of 1.6%. About 90% of the base-oils, which represent from 70 to 99% of all the lubricants, come from petrol. Therefore, 1% of world petrol consumption goes to this industry. Synthetic oils will contribute 10 % of base oils by 2015 [6]. Bio-lubricants share 1% of the market, with a growth rate of 5-8 % [7].

1.6 Future Lubricants

The future lubricant will be superior in performance, environmentally safe, sustainable, and compliant with modern legislations. The higher viscosity index and lubricity have allowed for a decrease in the required viscosity. This means lower energy losses. In addition, chemical stability and less volatility will decrease the incidents of leakage and frequent changes. These developments have already taken place in the present products of today's market. With a greater focus on the environmental aspects of new products, about 50 percent of a used lubricant returns back to the environment [6], due to evaporation, leakages, spills, and other mishaps, which pollute the air, soil and water. (See fig. 1.3) For this reason and others, there is a general trend in the world, among decision makers and pubic mediums, to follow more environmental approaches in industry. This trend is being translated into legislation day by day, adding more restrictions on conventional products, such as mineral lubricants, especially in some applications, where the damage has become intensified, like closed waters, lakes and rivers.



Figure 1.3: Fate of global lubricants after use in 2009

Biodegradability and lethal dose concentration (LD50, LC50) tests are important measurements to decide the lubricants' compliance with the environment restrictions. The biodegradability test was defined under different international standards, ASTM, such as D6731, D5864 and D7373. According to D6731/ 2011, "Bio-degradation of a lubricant, or the component of a lubricant, is determined by measuring the oxygen consumed when the lubricant or component is exposed to microorganisms under controlled aerobic aquatic conditions." [8]. LC50 & LD50 are the lethal concentrations or doses that cause death to 50 % of the tested animals group [9]. The animals are usually rats and mice, which can be exposed to the lubricant by skin exposure, an oral dose, or inhalation. This is decided based on the intended application and chosen medium, which could be via air, water, or direct exposure. The dose is calculated with respect to the animal's weight and the concentration by ppm.

Regardless of the environmental impact, mineral oil comes from a limited source, petrol. The confirmed and potential preserves are still under debate, but most sources say the prices will go up before we come to the end of the supply. This makes competitive technologies more feasible. The vegetable oils can not only deal with most of the concerns that have been mentioned above, but also satisfy most expectations regarding the performance of a modern lubricant. One of the main challenges with bio-lubricants is oxidation, so most bio-lubricants are being used for applications that do not require high temperatures. There are some successful attempts to modify bio-oils into more stable oils and use them in harsh conditions like those from internal combustion engines. [6] However, in terms of the limited supply, it is still more economically feasible to use them in applications with temperatures of less that $100 \ ^{o}C$.

1.7 Canola Oil in Canada's Economy

Canola oil is one of the vegetable oils that have been used commercially as a lubricant base for many applications. It is genetically improved from rapeseed and has the potential to be modified more to suit specific requirements. Seed oils and their products represent the largest crop trade in the world. While rapeseed production in Canada started in 1936, it became more widespread in 1942, in an effort to provide new sources for lubricants to war machines. Furthermore, the first genetically modified low Erucic rapeseed oil was produced in Canada 1968. The name "Canola" was adopted in 1978 to denote double-low Erucic acid rapeseed. These consecutive successes led Canada to be the largest exporter of rapeseed in the world [10].

Nowadays, the canola industry contributes \$15.4 billion annually to Canada's economy, and provides 228,000 jobs. Canada produced 9.0 million Tonnes of canola products during 2006, which reresents about 15% of global production and 75% of its trade. Only



Figure 1.4: Utilizations of canola oil

20 to 25 % of Canadian production goes to Canadians consumers. That represents 40% of the local vegetable oils market. Regardless of the saturation level of the domestic Canadian market, the edible market, even with the remaining 60%, does not satisfy the impetus plan that targets 15 million tons in 2015. It is obvious that exporting would sustain the development of the canola industry. In addition, diversifying the uses of applications for rapeseed oils would increase the stability of this industry. As a matter of fact, a significant portion of the future increase will be attributable to the bio-fuel sector [11]. The grease and lubricants industry, besides, could be promising consumers of canola oil.

1.8 Physical and Chemical Properties of Canola Oil

Canola oil comes from crushing the Brassica Seeds that belong to the mustard family. According to the canola council of Canada, canola oil is: "an oil that must contain less than 2% Erucic acid, and the solid component of the seed must contain less than 30 micro moles of any one or any mixture of 3-butenyl glucosinolate, 4-pentenyl glucosinolate, 2hydroxy-3 butenyl glucosinolate, and 2-hydroxy- 4-pentenyl glucosinolate per gram of air-dry, oil-free solid" [11]. As with most vegetable oils, canola oil is mainly a triglyceride of fatty acid chains. Fig (1.5) shows the molecular structure of the triglyceride, glycerol portion and oleic acid. The last one represents more than 60% of the fatty acids in canola oil; (see table 1.1) [12]. Table 1.2 gives the Triacylglycerol composition of canola oil [13]. The chemical composition is responsible for the thermal and oxidation properties of the oil [13, 14].



Figure 1.5: Molecular Structure of the main compositions in canola oil [14, 15]

Compared with mineral oils, canola oil has highly polar and larger molecules [18]; it has very good lubricity and a high viscosity index (VI); it has less volatility and a higher flash point; it has better detergent and anti- corrosion properties. On the other hand, canola oil has higher pour point and lower oxidation stability. Some physical properties of tested oils, such as density, thermal expansion, and surface tension, were measured and reported in the appendix.

1.9 Additives

The percentage of additives in a lubricant can be up to 30% [6], while the additives in tested oils varies from 5 to 10% [1]. Lubrication tasks exceed merely decreasing friction and wear; they involve such jobs as dissipating heat, conducting or insulating electricity,

1.9.	Additives
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Fatty acid	symbol	Formula	Wt (%)	No. of C
Palmitic	Р	CH3(CH2)14COOH	3.68	16
Oleic	0	CH3(CH2)7CH CH(CH2)7COOH	63.49	18
Linoleic	Li	CH3(CH2)4CH CHCH2CH CH(CH2)7COOH	20.05	18
Linolenic	Le	CH3CH2CH CHCH2CH CHCH2CH CH(CH2)7COOH	9.46	18
Stearic	S	CH3(CH2)16COOH	1.65	18
Eicosenoic	-	CH3(CH2)7CH = CH(CH2)9COOH	1.16	20
Arachidic	-	CH3(CH2)18COOH	0.51	20
Erucic	-	m CH3(m CH2)7 m CH= m CH(m CH2)11 m COOH	< 0.1	22

Table 1.1: Chemical composition of canola oil

Table 1.2: Triacylglycerol composition of canola oil

Triacylglycerol	POP	PLiP	POO	POLi	POLe	PLiLe	TOTAL
Mole fractions	0.009	0.0057	0.0909	0.0668	0.039	0.0105	0.9999
Triacylglycerol	SOO	000	OOLi	OOLe	OLiLe	OLeLe	TOTAL
Mole fractions	0.0214	0.23276	0.2409	0.1776	0.0756	0.0249	0.9999

removing foreign particles, and keeping them out. Usually, the base oil lubricant cannot satisfy all of these requirements. Thus, different packages of chemical additives are added to enhance the lubricant's functionality. While many of the additives are responsible for a significant part of the superior performance of modern lubricants, some of them, like heavy metals and polymers, account for the toxicity and biodegradability resistance [18]. Some indicators and techniques are used to measure and evaluate the performance of a lubricant, such as : Viscosity index (IV), IOS number, pour point, flash point, and seizure point. The additives include anti-oxidants, corrosion inhibitors, anti-foam agents, antiwear agents, viscosity modifiers, viscosity index improvers, detergents, and dispersants. As for viscosity, anti-wear agents, detergents, and dispersants, the natural properties of some bio-oils are good enough to work even without any additives. Moreover, the conventional additives would be not compatible with bio-oils, which means they would not be chosen for use with environmentally friendly bio-lubricants. A low amount of phosphate and phosphate esters can be used to enhance the degeneracy; sulphanates make good corrosion inhibitors; an amine phosphate compound is good for as antiwear, and silicon is a good anti-foam agent [18].

In our study, the additives in the lubricants are confidential information that is not intended to be revealed. However, no viscosity improvers were added and we may generally assume that the bio-lubricant behaviours are mainly inherited from the original chemical composition of the canola oil.

1.10 Lubrication Regimes

While Stribeck's curve (1902) explained the friction in journal bearings, it still insists on the main concept of the transition from one lubrication regime to another. The two main categories of lubrication regimes are hydrodynamic and boundary lubrication. In hydrodynamic lubrication, both sliding surfaces are separated completely by layer of fluid with more than $1\mu m$ of thickness [19]. The friction in this regime is very low, which is only due to the viscosity, so viscosity is the most vital property in this regime, besides the nature of the flow. On the other hand, we have the boundary regime, in which the sliding surfaces are much closer to each other, 1 to 10 nm. This narrow space is occupied by singular or multi-molecular layers. Thus, the viscosity does not become as important as in the previous regime. Instead, other physical and chemical properties of the oil, which affect how it reacts with metal surfaces, become more important. More details about the surfactant properties of the oil will be discussed later. Some other regimes could be classified in between boundary and hydrodynamic, such as elasto-hydrodynamic, in which elastic deformation becomes significant, which takes place between Non-conformal surfaces. The conformal surfaces fit each other so the engaged area keeps constant, as in a journal bearing. Non-conformal conjunction is like mating gear teeth [19]. Another regime that can be mentioned is the mixed regime, in which the hydrodynamic regime is mixed with the boundary regime. Figure (1.6), Stribeck's curve, plots the relation between friction coefficient and dimensionless Hersey number that is given as [19]:

$$H_s = \frac{\eta\Omega}{p} \tag{1.1}$$

where η is the dynamic viscosity, Ω is the rotational speed, and p is the pressure.



Figure 1.6: Stribeck's curve

From a practical point of view, a good lubricant is designed to deal with all regimes because, not only it is difficult to find a machine with one regime of lubrication, but the rubbing coupling itself can transit from one category to another. Figure 1.7 shows energy losses in the internal combustion engine [20], where the losses are due to different kind of regimes. In journal bearing, which shows a clear case of the hydrodynamic regime, the lubrication becomes mixed at low speeds.



Figure 1.7: Energy losses in the internal combustion engine

1.11 Surfactant Behaviour

Even during boundary lubrication, where the pressure is very high and the surfaces are very close to each other, there is still a layer of single or multi- molecules in thickness separating which decreases the wear and friction significantly.



Figure 1.8: Adsorption mechanisms in fatty acids on steel surfaces

The molecular self-assembly depends on the material nature of the lubricant and rubbing surfaces. There are different mechanisms by which these films can format, as listed in reference [21], and as follows: 1- physical adsorption; 2- chemical adsorption; 3-chemical reaction not involving substrate; 4- adsorption; 5-chemical reaction involving subtrate. Reference [17] further more elaborates on physical adsorption, which includes capillary, electro-static, and Van der Waals forces. Increasing the stability and thickness of the self-assembled layer will reflect positively on the lubricat's performance. Besides infrared and X-ray spectroscopy, there are many tools that can be used to study this phenomenon, such as probe microscopy, which includes atomic force microscopy, a friction force microscope, a chemical force microscope, an interfacial force microscope, and a surface force apparatus. Fig 1.8 shows the adsorption mechanism of fatty acids on to steel surfaces [21]. While new advanced technology revealed much about previously unexplained phenomenon, we still have a long way to go. There is still difficulty both in explaining the tribological behaviour, and in matching between its microscopic and macroscopic aspects [17]. In this research, the rheometer will be represented as a new tool to be used to characterize the surfactant behaviour of the lubricant.

1.12 Liquid Crystals [2, 22]

Liquid Crystals (LCs) are anisotropic, viscoelastic materials with that combine a fluidlike with crystal-like properties. Liquid crystal material can improve the lubricity of a lubricant, and while it is not yet fully understood how they work, there are some explanations available, due to the orientation and the surface activities. With respect to different flow directions, the anisotropy of the viscosity coefficient, is a unique property of the liquid crystalline phase. The ability of liquid crystalline materials to form ordered boundary layers with good load-carrying capacity, while lowering the friction coefficients, wear rates, and contact temperatures of sliding surfaces.[2]

The rod, nematic liquid crystals consist of cylindrical molecules more or less aligned in a common direction, represented by the uniaxial director n . Some materials could have
more than one phase of liquid crystals, according to temperature and/or concentration. The liquid crystals can have order in position and orientation; which is called smectic. Fig (1.9) illustrates both the smectic and nematic phases.



Figure 1.9: Nematic and smectic order of liquid crystalline phases

Chapter 2

Methodology

2.1 Literature Review

2.1.1 Rheometry of Bio-lubricants and Low Viscous Materials

The research regarding lubrication problems has focused mainly on experimental work on the oil's tribological performance, and the CFD modeling of hydrodynamic friction that implemented viscoelasticity. Meanwhile, applying rheometery dynamic tests on oils has been limited. Rotary rheometers have been used more commonly to test the oils at moderate shear rates. Both capillary rheometres and falling ball viscometers have been used to study high shear and high pressure, respectively. Considering the problem of lubrication generally, the studies that addressed the viscoelasticity in lubricants focused more on greases and emulsions.

2.1.1.1 Rheometry of Bio-oils

The bio-hydraulic oil that was tested in this research, however, was studied before rheologically [23]. Some vegetable oils, including canola oil, showed strong shear thinning at a shear rate of 100 s^{-1} and lower [24]. Inexplicably, the shear thinning increased with temperature, which questions the stability of the experiments. While the previous research used viscometer, we used an advanced rheometer, about which the manufacturer says it has the lowest inertia motor in the market. However, it became difficult to maintain stability at a very low viscosity. Other studies focused on the correlation between the fatty acids composition of the bio-oils and their viscosities, within a temperature range from 20 to 100 $^{\circ}C$ [13, 25, 26]. While the studies [13, 26] used capillary viscometers, a rotating viscometer was used in [25]. It was found that the viscosities of pure saturated triglycerides follow the second order function of the carbon number quite well. The behavior of different vegetable oils at low temperatures, i.e., of up to -40°C, was studied using a rotational controlled strain rheometer [27]. The fluidity was remarkably improved by using viscosity modifiers, where the pure point decreased from -18 to -36° C. While the pressure decreases the density and increases the viscosity, pressurized corn oil, using compressed CO2, showed the opposite, due to the dissolution of CO2. The tested pressure went up to 12 MPa in a pressure cell combined with a rotary rheometer [28]. A mixture of soybean and commercial oils was optimized using a rotary rheometer to achieve the desirable viscosity index (VI) [29].

2.1.1.2 Rheometry of Low Viscous Liquids

Due to the low torque and instability associated with low viscosity, the practice of using rotary rheometers to conduct dynamic tests in the field of lubricants is done almost exclusively on greases, emulsions, and gels that have higher viscosities [30, 31, 32]. While these limitations can be extended to low viscous materials generally, some effort has nonetheless been made to try and do further testing. The results of a frequency sweep test of lubricant called perfluoropolyether are represented in reference [33]. The perfluoropolyether lubricant had a viscosity of 0.08 Pas at 10°C. The lubricant did not show non-Newtonian behavior at a shearing rate less than $10^3 s^{-1}$. Further, G' was inversely proportional with temperature, between 10 and 30°C and almost constant between 30 and 50°C. The frequency domain was between 0.04 and 4 Hz. To our knowledge, the material with the lowest viscosity, which had been tested under SAOS using the rotary rheometer, was cholesteric liquid crystals, [34]. The viscosity was about 0.04 Pas, which is equivalent to tested oils in this research at 40°C.

2.1.1.3 Rheometry of More Viscous Related Materials

Regarding more viscous materials, heavy oil, 2 Pas at 80°C, was tested under a wide range of frequency, i.e., 0.01 to 100 Hz [35]. Crystalization in the formulation of palmitic fatty acid was studied using a frequency time sweep [36]. Palmitic fatty acid is one of the composite components of canola oil. The waxy appearance in crude and paraffin oils was investigated using viscometry tests [37, 38].

2.1.1.4 Rheometry of Engine Oils

More intensive work has been focused on engine oil, especially at high pressure and shear rates. A fall object viscometer was used to study the effect of pressure up to 1.2 GPa [39, 40]. Oil viscosity responded to extreme pressure more than exponentially increasing. Using a capillary tube, at 38°C, poly alpha olefin showed shear thinning at the high shear rate of 10³ to 10⁷ [39]. There was no regaining of the plateus at the end of the curve. It is worth mentioning that slipping could take place at a high shear rate. The other study, which used the capillary tube rheometer, found that pressure has a strong influence on the viscoelastic properties of multi-grade oils [41]. The work done at Shell's research center on multi-grade oil 10W50 showed shear thinning between two plateau regimes. The shear thinning appeared earlier as the temperature decreased [42]. The positive viscoelasticity impact on the performance of multi grade oil was demonstrated using rheometery and tribology simulation [43]. The velocity field of multi-grade oil within an eccentric cylinder was determined using a Doppler laser gauge. This unique effort aimed to validate upper-convected Maxwell model in viscoelastic lubrication [44].

2.1.2 Rheometry Errors

Some of the measuring errors when rotary rheometer is used are more associated with low-viscous liquids rather than thick and strong materials. The most common are: the gap errors at very small gaps, liquid inertia contribution, secondary flow due to the wide gap or misalignment, and unsteady rheometer. Further, the low viscous sample could be affected by heat dissipation and wall-slip to a lesser extent. Thus, studying these errors and quantifying them has been drawing many researchers' attention. In effort to achieve very high shear rate within a thin gap, the gap errors were studied extensively in parallel plate geometry. The errors in gap size were attributed to misalignment of the parallel plates, and contribution of the air pressure during the squeezing for gap zeroing, [45, 46] the liquids' inertia effects within concentric cylinders and wide gap were studied [47, 48]. The contribution of the liquid inertia to storage modulus in parallel plate and concentric cylinders measuring systems was quantified also [49]. Non-parallelism in parallel plate measuring system was studied theoretically in case of Newtonian fluid [50]. The unsteady rheometery which has significant impact on dynamic tests was studied theoretically and experimentally [51, 52] It was found that time response of the rheometer increases with inertia and decreases with the sample viscosity, also the maximum frequency was determined based on the coupling between the rheometer and the sample. Wall-slip was measured experimentally, and it was found that it was important as it could affect the CFD simulations according to defined boundary conditions significantly [53]

2.1.3 Mathematical Model

Mathematical work on lubrication has been focusing on the hydrodynamic lubrication with more emphasize on the flow within eccentric cylinders and journal bearings. A remarkable number of researches modeled lubricants as non- Newtonian fluids and with much less as viscoelastic lubricants. D. Grecov simulated the non-Newtonian flow within eccentric cylinders using stream-tube method [54]. T.N. Phillips published number of papers to simulate the flow within dynamically loaded journal bearings using Oldroyd-B and PTT models [55]. H. Boucherit after he studied different forms of the Maxwell models concluded that there is still a gap between viscoelastic mathematical models and experimental data for real lubrication cases [56]. This questions the credibility of applying the known viscoelastic models on the flow of lubricant within a journal bearing. There is a few works in that aspect, reference [44] is one of them. Even though the validation of Maxwell model was proved according to that research, still the investigated case was flow within eccentric cylinders rather than real case of journal bearing. Meanwhile, there is a new effort to use the molecular dynamic to simulate very narrow gaps [57].

2.1.4 Thermal Analysis

The Differential Scanning Calorimetry (DSC) technique has been used widely to study bio-oils for different purposes. It was successfully used to study the waxy appearance in vegetable oils, where two peaks on the DSC curve were identified at low temperatures; these were attributed to the oil's molecular structure and two different forms of crystalline phases [58]. DSC studies on different vegetable oils have also revealed a connection between their thermal behavior and chemical compositions [59, 60]. DSC was used, as well, to investigate and improve the oxidation stability of different vegetables oils, such as soybean, safflower, sunflower, and mustard oil [61, 62], and to diagnose sedimentation in canola oil [63]. Other research found a connection between rheology and DSC, where transition points appeared on the curves of shear viscosity, storage modulus, and heat [64, 65].

2.1.5 Bio-lubricants Tribology

It is well known that vegetable oils have good lubricity, due to their triacylglycerol structure. A study on Palm oil showed that it has a lower specific wear rate compared with commercial mineral oil [66]. In contrast, coconut oil has a larger wear rate compared with commercial oil, as shown in an extreme pressure test [67]. It should be taken into consideration that most of the researches on vegetable oil used just raw oils, whereas the commercial oils are enhanced with many improving packages. These improving packages came as a consequence of the long cumulative experience of giant companies that specialized in the field of lubricants. The performance of saturated stearic acid and unsaturated linoleic acid as additives to improve lubricity was studied [68]. The experiments were done on both the nano and micro scales. While the mechanism of how these materials adhere to steal and form self-assembly monolayers is defined, it is still not clear why it is time dependent.

2.1.6 Liquid Crystal Additives

While many researchers have been studying the tribological effect of liquid crystals on oils, they were mainly on mineral oils; far fewer have been done on bio-oils.

2.1.6.1 Liquid Crystals with Water

Alkyl polyglucosides, were tested as an additive to water [69]. The tribological experiments showed a reduction in friction of up to 7 times. Additionally, several other tests were conducted, including: surface tension, wetting angle, light diffusion and viscosity, atomic force microscopy, polarized light microscopy, and X-ray spectroscopy, which indicates the existence of micelles and liquid-crystalline structures.

2.1.6.2 Liquid Crystals with Mineral Oils

A study on six types of cholesterical liquid-crystals with four mineral oils [70], found improvements in wear reduction over all of them. Also, it gave a chemical explanation to the deformation of the monolayer and the advantage of cholesteryl chloride over the others, due to its chlorine content. Another researcher [71] studied 14 additive materials from different families of liquid crystals. They were tested with different oil bases on rubbing couple of steel-steel, and the results were positive for all of them, over all tested temperatures (from 27 to 50 °C). Also, they found that the change in viscosity had little effect on the results. In an attempt to achieve ultra-low friction, a mesogenic fluid mixture was used [72]. Comparing the tribological performance of ionic and neutral liquid crystal additives, all experiments showed that ionic liquid crystals have less wear [73]. In a related effort, 7 different ionic liquid crystals were tested [74]. One of them was 1-butyl-3-methylpyridinium with an oil base and Aluminum-steel contact coupling. They showed positive improvement, which the researchers attributed to the effectively adsorbed lubricating layers due to the reaction between the steel and ionic liquid crystal.

2.1.6.3 Liquid Crystal with Bio-oils

There is limited number of researches that deal with liquid crystals as additives to bio-lubricants. 5% of boric acid was used with canola oil and resulted in a superior lubricant, even over commercial lubricants [75]. The relative improvement with pure canola oil itself was not mentioned. The impact of ionic liquid crystals on different oils, including bio-oils, was investigated [76]. The very low friction coefficient indicates that the friction is either hydrodynamic or mixed. It is known that the viscosity is very important in these regimes, where the tested samples have wide variations in viscosity. Moreover, there is a significant contrast in the results among canola oil, safflower oil, and vegetable oil, especially the fact that canola and safflower oil have similar chemical compositions.

2.2 Materials



Figure 2.1: Greenland oils

Greenland Corporation is a Canadian company located in Calgary, Canada. They manufacture bio-lubricants from canola oil. They have 14 different products. In this research, three of their products were tested: hydraulic oil, gear oil, and chainsaw oil. As well, a commercial mineral hydraulic oil was tested, as shown in figure (2.1). With the goal to compare these oils during the period of the study, only two batches of these oils were tested and no change was noticed. Neither the consistency of lubricants nor their chemical composition was investigated. The company says it has restrict quality control on the raw materials, although they are still biomaterials and some variations are not very far from. In addition, two types of liquid crystals from Sigma Aldrich were used as additives: 97% cholesteryl chloride, 1-butyl-3-methylimidazolium (tetrafluoroborate). The molecular structures of both liquid crystals are illustrated in figure (2.2). Silicon oil, in compliance with United Kingdom standards, was used as a calibration oil to check the accuracy of the rheometer, periodically. (See figure (2.3))



Figure 2.2: Liquid crystals additives



Figure 2.3: Calibrating oil

2.3 Rotary Rheometer

The rotary rheometer is often used, due to its advantages: it requires only a small sample size; it is easy to apply certain conditions on the sample such as temperature, electric field, and UV exposition; it works continuously, so it can run as long as the nature of the sample allows. While researchers can classify rotary rheometers based on its controlling modes, i.e., rate control or stress control, these are not such a distinguishing feature, as many modern rheometers can work in both modes. It is more pertinent to classify rotary rheometers based on their torque sensor locations. While on single head rheometers, the torque sensor and the motor are located in one side, in the separated heads rheometer, they are separated by the sample. While the first setup is simpler and more flexible



Figure 2.4: Illustrative schematic diagram of single head design of a rotary rheometer

for applying different environment control facilities, it has to deal with motor inertia and bearing noise, which affect its accuracy. Figure (2.4) provides a general illustrative scheme of the single head design.

The rheometer used in most rheometery experiments in the current research was the Kinexus brand, manufactured by the Malvern company as is shown in figure (2-5). It has dual controlling mode capabilities for both shear and stress, it is a single head, and provided with porous air-bearing.

The two major sensors in the rheometer are the position and torque sensors. The position sensor was not a concern for us. For example, assume we are applying a shear rate of 10^{-2} , using a cone and plate of 20 mm radius / 1° angle, the angular velocity under these severe conditions would be around 2.7 X 10^{-5} rad/s, while the encoder in the Kinexus rheometer has a resolution of less than 10^{-8} rad/s. The challenge was measuring



Figure 2.5: Kinexus rheometer

the torque. Even though the rheometer we used has a highly sensitive sensor, namely 5 X 10^{-8} Nm, it has to deal with the noise coming from the inertia and porous air-bearing. In the case of a highly sensitive sensor, the accuracy is limited to unpredicted noise rather than the accuracy of the torque sensor. In this respect, the software, which has to deal with the corrections as well as the precise controls, especially in dynamic tests, is just as important as the hardware, maybe more. Not all the information about the software was available to us. The lowest torque considered in the reported results was 10^{-6} Nm. The rheometer we used did not measure the gap directly as the most rheometers on the market, generally. Instead, it is the displacement of the motor that is measured, and the zero gap is recognized by the normal force. Even the very sensitive displacement sensor, 10^{-7} m, cannot guarantee error-free gap measurements at small gaps. It is worth mentioning that, while gap error due to inaccurate gap size can change the values, behavior of the oil remains consistent. Meanwhile, errors due to the imperfect shape of the geometry or non parallel could also cause changes in the oil's behavior, because of the secondary flow. The motor inertia of the Kinexus rheometer is 13µN.m.s, which is the smallest inertia of any rheometer motor on the market, according to the manufacturer. Further, the maximum torque claimed is 200 mNm. In practice, it could be above or lower than this, depending on the rotation speed. We also noticed that the rheometer has high and stable acceleration compared with other brands. However, we do not have a complete understanding of the rheometer's dynamic response, but we relied on some measurements provided by the software, which will be discussed later in this chapter.

2.4 Measuring Systems

Different measuring systems can be used by the rotational rheometer, based on the properties of the materials and the purpose of the test. It is desirable that the result is independent of the geometry, which is not always the case. The cone and plate, concentric cylinder, and parallel plate measuring systems are described by ISO 3219(1993), 6721-10(1999) [77]. The advantage of these geometries is that the applied shear is defined across the sample. However, the shear is constant only in the cone and plate, and in the concentric cylinder. The varying shear rate with diameter in flat plate measuring systems adds complexity to the calculations when the viscosity is shear dependant. Actually, we used flat plate geometry in most of the experiments because of the ability to control gap size. Figure (2.6) is a schematic drawing for the flat plate system.



Figure 2.6: Parallel plate measuring system

The upper disk is moving while the lower is fixed. Both shear rate and shear stress are required to calculate the apparent viscosity (Eq. 2-1). The shear rate varies linearly from zero at the center to maximum at the rim of the plate, which is determined by the following equation:

$$\eta = \frac{\sigma}{\gamma^o} \tag{2.1}$$

$$\gamma_R^o = \frac{R\Omega}{h} \tag{2.2}$$

Where η is the viscosity, σ is the shear stress, γ^o is the shear rate, γ_R^o is the shear rate γ_R^o is the shear rate at the rim of the geometry, R is the radius of the geometry, and h is the gap size, Ω is the angular velocity. In the following, the shear stress is a function of the radius. The shear stress on the rim can be obtained from the integration over the radius[45, 78]:

$$\sigma_R = \frac{M}{2\pi R^3} \left(3 + \frac{dln(M)}{dln(\gamma_R^o)}\right) \tag{2.3}$$

Where M is the measured torque. To solve the above equation, the relation between M and γ_R^o . needs to be determined first, which means adding corrections to the results, unless the tested material is a Newtonian fluid. In many cases, when the tested material exhibits shear thinning or thickening, it can be approximated to power-law. Accordingly, in the case of a Newtonian fluid and power-low material, Eq. (2.4) can be used to calculate the viscosity [45, 78]:

$$\eta = \frac{3Mh}{2\pi R^4 \Omega} (1 + \frac{n}{3}) \tag{2.4}$$

Where n is the power-law constant, which is one, in the case of a Newtonian fluid. It should be pointed out that the rheometer software calculates the viscosity based on the Newtonian equation, and considers the shear rate at 0.75 of the radius.

2.5 Short Amplitude Oscillation Shear (SAOS)

Just as Newtonian fluid obeys Newton's laws, Hookean solids obey Hooke's laws. This implies that Hookean solid is linear elastic. Some materials, which are called viscoelastic, have the ability to dissipate energy as Newtonian fluid and store it as a Hookean solid. The SAOS test can demonstrate the two components of the tested material.



Figure 2.7: Time dependant functions of SAOS, (shear rate, strain and stress)

Considering applying an oscillatory shear to the sample instead of a continuous shear, according to the following equation [77, 78, 79, 80]:

$$\gamma(t) = \gamma_A \sin(\omega t) \tag{2.5}$$

Where γ_A is the shear amplitude, ω is angular frequency, and t is the time. Consequently, the shear rate precedes the shear strain by $(\pi/2)$ or follows a cosine function, as is shown in figure (2.7). The response of the sample or shear stress depends on the properties of the material being tested. If the sheared material was an ideal elastic solid, the shear stress would be in phase with the strain. If the sheared material was ideal viscous fluid, the shear stress would be in phase with the shear rate. The viscoelastic material responses fell somewhere in between with phase angle (δ), which is between zero and ($\pi/2$). Besides the phase angle, the measured torque or calculated shear stress amplitude imply two important measurements; the storage modulus (G'), which is a measure of the elastic part; and the loss modulus (G"), which is a measure of the viscous part. In a similar way, the control mode could be based on shear stress and the measured property is the strain amplitude and plus the phase angle.

$$G^* = \frac{\tau_A}{\gamma_A} \tag{2.6}$$

$$G' = \frac{\tau_A}{\gamma_A} sin(\delta) \tag{2.7}$$

$$G'' = \frac{\tau_A}{\gamma_A} \cos(\delta) \tag{2.8}$$

Where G^* is the complex modulus. The previous measurements can be expressed in complex numbers notations, as follows:

$$G^* = G' + iG'' \tag{2.9}$$

2.6 Mathematical Model [80]

The Newtonian fluid constitutive equation is expressed as follows:

$$\bar{\bar{\tau}} = \eta \bar{\gamma}^o \tag{2.10}$$

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$$\bar{\gamma^o} = \nabla \bar{v} + (\nabla \bar{v})^T \tag{2.11}$$

$$\overline{\tau} = \begin{pmatrix} \tau_{xx} & \tau_{xy} & \tau_{xz} \\ \tau_{yx} & \tau_{yy} & \tau_{yz} \\ \tau_{zx} & \tau_{zy} & \tau_{zz} \end{pmatrix}$$
(2.12)

Where $\overline{\overline{\tau}}$ is the stress tensor, $\overline{\overline{\gamma}^o}$ is the rate of strain tensor, and $\overline{\nabla v}$ is velocity gradient tensor. For non-Newtonian fluids, the viscosity is a function of the shear rate, so the constitutive equation can be generalized as follows:

$$\bar{\bar{\tau}} = \eta(\gamma^o)\bar{\gamma^o} \tag{2.13}$$

The function $\eta(\gamma^{\circ})$ which could be 'power-law' can represent a non-Newtonian fluid accurately only when the effect of the shear history or the memory is neglected. In case of viscoelastic materials, it is valid only when the flow is steady and time independent. The Maxwell model incorporates the memory effect by including the time derivative of the shear stress.

$$\ddot{\overline{\tau}} + \lambda \frac{\partial \bar{\overline{\tau}}}{\partial t} - \eta_o \gamma^o = 0$$
 (2.14)

[Maxwell model, integral form]

$$\bar{\bar{\tau}}(t) = -\int_{-\infty}^{t} \left[\frac{\eta_o}{\lambda} e^{\frac{-(t-t')}{\lambda}}\right] \bar{\gamma}^o(t') dt'$$
(2.15)

Where λ is the relaxation time of the material, η_o is zero shear viscosity, t is time of interest, and t' is a dummy veriable denotes the past times. The model was built on the basis of its resemblance to the mechanical model, spring dashpot as is illustrated in

figure (2.8)



Figure 2.8: Viscoelastic material is resembled to mechanical model of spring and dashpot in series

While the spring represents the elastic part, which has the ability to store energy and exert resistance to deformation proportional with the strain amplitude, the dashpot represents the viscous part, which dissipates energy and resists deformation proportional to the strain rate. Applying Maxwell model on the SAOS, which is the simple shear rate, gives:

$$\bar{\bar{\tau}}(t) = -\int_{-\infty}^{t} \left[\frac{\eta_o}{\lambda} e^{\frac{-(t-t')}{\lambda}}\right] \begin{pmatrix} 0 & \gamma_A^o \cos(\omega t') & 0\\ \gamma_A^o \cos(\omega t') & 0 & 0\\ 0 & 0 & 0 \end{pmatrix} dt'$$
(2.16)

$$G''(\omega) = \frac{g\lambda\omega}{1+\lambda^2\omega^2}$$
(2.17)

$$G'(\omega) = \frac{g\lambda^2\omega^2}{1+\lambda^2\omega^2}$$
(2.18)

2.7 Uncertainty

With low viscous and low viscoelastic materials, trivial errors can become significant. Thus, we paid carful attention to insure a high level of accuracy, which meant we had to take a number of approaches:

- 1. We were careful that all the experiments conditions fell within the rheometer real capabilities, which are: maximum torque at high rotation speed; lower torque at a low angular speed; maximum rotation speed; maximum stable frequency, acceleration time; and the lowest temperature at a high shear rate. However, we did not need to exceed all of these limitations in most cases, except the low torque and high frequency, which were always a challenge we had to overcome
- 2. The most common errors have characteristic signatures on the results. Observing any of these patterns is a prompt to investigate for errors.
- 3. In the case of the comparison between the bio-lubricant and Silicon oil and engine oil, where the first one is considered a Newtonian fluid, the second one is considered as a dilute polymer solution. We think the comparable viscoelasticity is more meaningful than the numbers themselves.
- The rheometer software has many measurements that alarm some types of errors. The most important three of these warnings will be detailed.

2.7.1 Software Error Measurements [81]

2.7.1.1 Steady State

Steadt state indicates the equilibrium, which is determined by two different equations, depending on the control mode. It should stay around (1.0) regardless of the applied equation or control mode. The test time could be decided automatically based on the

steady state, but it was set manually in most of the experiments we reported. Meanwhile, we were careful to make it long enough to preserve an acceptable steady state. The equations that determine the steady state are:

$$SS_{CS} = \frac{dln\gamma(t)}{dln(t)} - \frac{dln(\sigma)}{dln(t)}$$
(2.19)

$$SS_{Cr} = 1 - \frac{dM}{dt} - \frac{t_i}{t_s} \tag{2.20}$$

where SS_{CS} is steady state measurment in controlled stress mode, SS_{CR} is steady state measurment in controlled rate mode, t_i is integration time, and t_s is sample time.

2.7.1.2 Harmonic Distortion

This is the measurement of how the input and output signals in SAOS are sine functions alike. The harmonic distortion was lower than 5% in all of the reported results.

2.7.1.3 Inertial Effects Dominating

This warning appears when the phase angle is close to 90° , and the elastic contribution is too small to be accurately considered.

2.7.2 Gap Accuracy

The displacement sensor does not measure the gap directly, but measures the head movement instead. Thus, some gap errors are expected, which become more significant at the very small gaps. Assuming the gap error is constant, which is not always the case, it can be extracted from the following equation [45]:

$$\eta = \eta_m \frac{h_m}{h_m + \varepsilon_q} \tag{2.21}$$

35

where η_m is the measured viscosity, h_m is the measured gap, and ε_g is the gap error. Figure (2.9) shows the measured and corrected viscosity of bio-hydraulic oil. Accordingly, the error in the viscosity varies from 2.3 to 3.5 % at gaps 0.3 and 0.4 mm, respectively, which were the most used ones.



Figure 2.9: Viscosity correction due to the gap error, bio-hydraulic oil at 20°C

2.7.3 Accuracy Versus Shear Rate

In an effort to investigate shear thinning or thickening, the viscosity of the oils tested was measured against the shear rate, as will be presented in (Chapter 3). For the purposes of validation, the same experiment setup was applied to the silicon oil, standard oil, as shown in figure (5.10). The errors in the average viscosity at 30°C were less than 1 %. Slight shear thinning could be observed, even in the silicon oil case because of the secondary flow. In a comparison, this level of change in viscosity of the tested oil will not be considered.



Figure 2.10: Viscosity versus shear rate, standard oil

2.7.4 Repeatability

The rheometer software is still being evolved by the manufacturer, and the rheometer was used by different researchers. Thus, the accuracy of the gap was checked periodically, using the tested oil itself, and the measured viscosity was checked periodically using standard oil, especially before the viscometery experiments. According to the experiments done on standard oil, we assume the error of measured viscosities to be within 2%. The tolerance in the measured viscosity at the same temperature and shear rate is not more than 1%. The source of any non-repeatability most probably came from how the sample was trimmed or how the sample filled the gap, since it is a manual process. Where the G' depends on the delicate microstructure of the bio-oils, the repeatability in the SAOS tests was more concerning. As it will be presented, however, the reported results were estimated to be stable by 95%. Six different experiments at three different gaps gave a variance from 2.3 to 16.5%.

Chapter 3

Rheological Characterization

3.1 Overview

The best experimental conditions are the closest ones to real case, which is not always possible. Designing a good rheology experiment requires a solid knowledge about the concerned material, working conditions, and testing equipment. Our knowledge about the materials and the equipment has been developing in time for two reasons. A similar study on the same type of the materials was not available, especially with this extend. Estimating the real capabilities of rheometer is more than considering the named specifications, which are not detailed to cover every scenario, specifically. Consequentially, the reported experiments are the final version of our developing experience. Generally, the rheological experiments presented here can be classified into main categories; the more commonly used ones are: the viscometry and the SAOS tests. As well, the following complex procedures and specific purpose experiments were designed to answer specific questions:

- The viscometery experiments include testing the single shear rate at different temperatures, and the rising shear rate at constant temperatures.
- The SAOS experiments include shear amplitude sweeps and frequency sweeps at different temperatures. Only the results that were estimated to have reached a stability state with a reasonably low scattering will be presented.
- The complex procedures consisted of sequential experiments, for instance, different

patterns of shear rates at different amplitudes of oscillation time sweep tests, and combinations of the two. These tests were used to investigate time dependent and structure recovery.

• Special experiments were designed for certain purposes that combined using high pressure, polarized light microscopy, different gap sizes, and different geometry materials.

3.2 Viscometery

3.2.1 Viscosity Versus Temperature

The tested bio-lubricants in the present study do not contain any viscosity improvers. The investigated temperature domain varies from 0 to $100^{\circ}C$ besides being a reasonable range from a practical aspect; it is also a stable range for the rheometer temperature control. The same sample was tested at different temperatures, from 0 to $100^{\circ}C$, every time. It was given 5 minutes to stabilize under the aimed temperature, and it was sheared at constant shear rate (10 /s). The hysteresis effect due to the temperature change was neglected, as it was not thought to be significant. Figure (3.1) summarizes the results of three bio-lubricants and commercial mineral hydraulic oil tests. In terms of thermal stability, all of the bio lubricants have advantages over commercial mineral hydraulic oil. Both the bio- hydraulic and bio-gear oils followed similar patterns and have close viscosity along the tested domain, whereas the bio-chain saw oil deviates from them at temperatures lower than 20 C. It was noted that one exponential equation could not interpolate the viscosity across the entire temperature range, accurately. The same behavior appears in other researchers' results of canola and other vegetable oils [13, 26] without mentioning it explicitly. The same behavior was also found in other work on crude oil. This was attributed to the wax appearance around 45°C [37]. Similarly, all tested oils, both bio and mineral, showed the same behavior. In order to investigate the points of change, where the oil started to deviate from the exponential function, viscosity at low and high temperatures was interpolated by different exponential equations, as is shown in figure (3.2). The intersection between the two equations was considered as the changing point in the oil's behavior. It varied from 38 to 48 °C; the highest temperature was with the bio-chain-saw oil.



Figure 3.1: Viscosity versus temperature of different oils

To increase the credibility of the interpolated equations, other equations were tested. The best fits were achieved using double exponential equations. Figure (3.3) shows the improvement in credibility due to the double exponential function. The constants of these equations are listed in table (3.1)



Figure 3.2: Failure of single exponential function



Figure 3.3: Credibility of double exponantial function in representing the viscosity change with respect to temperature of bio-hydraulic oil

$\eta = ae + ce$						
	oil	a	b	с	d	Tested domain
1	Bio-hydraulic oil	0.20848	0.06574	0.04112	0.01781	$\left[0^{o}C \sim 100^{o}C \right]$
2	Bio-gear oil	0.22883	0.0701	0.05265	0.02006	$\left[0^{o}C \sim 100^{o}C \right]$
3	Bio-chain saw oil	0.09093	0.13744	0.10063	0.01274	$\left[0^{o}C \sim 20^{o}C \right]$
4	Bio-chain saw oil	0.18533	0.07195	0.0621	0.02215	$\left[20^{o}C \sim 100^{o}C \right]$
5	Mmineral hydraulic oil	0.41847	0.08351	0.05605	0.02344	$\left[0^{o}C \sim 100^{o}C \right]$

Table 3.1: Constants for double exponential regression $m = a e^{-bT} + c e^{-dT}$

3.2.2 Moderate Shear Rate

Shear ramp tests were conducted several times on the same sample at different temperatures, from low to high; also the shear increased according to the logarithmic step. The results were plotted in figure (3-4). No reliable indication of shear thinning or thikenning was noted unless in case of bio-chain saw oil at $0^{\circ}C$ which is still slight also. The very slight changes at high and low shear rates could be attributed to secondary flow, heat dissipation, and stability. The same slight change could be measured in silicon oil also, which is a Newtonian oil. It seems that polymer improvers were avoided in the commercial mineral oil in order not to affect its degradability. Consequentially, the assumption of vegetable oils as Newtonian fluids can be expanded to include tested bio-lubricants. It should be pointed out that the typical shear rate in pipe flow is 10° to 10^{3} , whereas the typical shear rate with lubrication varies from 10^{3} to 10^{7} [79]. Thus, further steps were taken to test the bio-hydraulic oil at a high shear rate, and compare it with commercial engine oil.



Figure 3.4: Viscosity versus shear rate at different temperatures. a) bio-hydraulic oil. b) mineral hydraulic oil. c) bio-gear oil d) bio-chain saw oil

3.2.3 High Shear Rate

An apparent contrast between engine oil and bio-hydraulic oil is illustrated in figure (3.5). Even though the engine oil is a diluted polymer solution, the shear thinning was obvious at a high shear rate that agrees with reference [42]. Figure (3.6) represents the normal force versus the shear rate. While in the case of the engine oil, the normal force increased with respect to the shear rate, in the case of the bio-hydraulic oil, the normal force stayed under zero. The negative normal force was due to the inertia effect. The assumption that bio-lubricants are Newtonian fluids is still valid at high shear rates, also. However, this is a trivial solution because it does not give much information, or tell us what the difference between oil and water is. Thus, we recognized the need for further investigation into the viscoelasticity of bio-lubricants, and the findings will be presented.



Figure 3.5: Viscosity at high shear rate, bio-hydraulic and engine oils



Figure 3.6: Normal force at high shear rate, bio-hydraulic and engine oils

3.2.4 Yield Stress

Yield stress was measured only in bio-chainsaw oil, at temperatures under 20° C. Interestingly, this is the same area in which bio-chainsaw oil differed from other oils. More work on bio-hydraulic oil will reveal the existence of yield stress, but it takes a longer time to build up. In fact, yield stress is the first sign of non-Newtonian behavior. It was found that temperature history influenced the results, but faded with time. Yield stress is demonstrated in the viscosity-shear stress diagram, as shown in figure (3.7). The same sample was tested at different temperatures, from high to low, after it was given 5 minutes to rest. Calculated yield stresses using linear regression are 0.0177 & 0.008 Pa at temperatures 0 & 5° C respectively.



Figure 3.7: Yield stress in bio-chainsaw oil

3.3 Small Amplitude Oscillatory Shear (SAOS)

Even though the focus was on bio-hydraulic oil, different oils were tested for the purposes of comparison and validation. Assumedly, all bio-lubricants behave similarly. The behavior of bio-oils is complex. The oils are delicate materials, i.e., they are time dependent, path dependent. Only the results that were convincingly repeatable and explainable are reported. However, it should be stated that there is no guarantee of getting the same results again, unless the same circumstances are provided. Furthermore, in many cases the used rheometer capabilities were taken to the end of range; another rheometer with lower specifications would not be able to get the same results, accurately. We were careful to use the same experiment setups on the different samples, especially when comparison was intended. Moreover, an effort was made to unify the preconditions, as listed below:

- Temperature, a new sample for every temperature was used, to avoid any hysteresis effect, unless the test itself required temperature changes. Five minutes was given to

samples to stabilize. The cooling and heating rates were neither taken into account nor studied.

- Surface conditions; it was noted that bio-lubricants gave different results according to how the geometries were cleaned, i.e., with a paper towel, detergent, or ethanol. The sonication bath was not available in the lab, so the geometries were cleaned using ethanol and then with flame several times until geometry cleanness became obvious.

- Pre-shear. Two types of oscillatory procedures were conducted in this research: either continuous oscillation or oscillation with shear intervals in between. It was noted that every shear could lead to different states in values or patterns. Figure (3.8) sketches the multi-oscillation procedure. The shear in the interval periods was set to zero in the case of the reported results.

- Time: it was found that G' is time dependent. All the following experiments, which are not functions of time, were performed 5 hours after applying the sample, approximately. It is estimated that bio-hydraulic oil reached 95% of its steady state after 5 hours, with a gap of 0.3 mm. This estimation is based on polynomial extrapolation. A test on time dependence will be presented.



Figure 3.8: Illustrative input signal of multi oscillation procedure

3.3.1 Oscillation Amplitude

This test is an essential step for further tests to determine the limits of linear viscoelasticity, which was found to be 10% according to figure (3.9). The linear viscoelasticity, where G' is independent of oscillation amplitude, could be lower than 10%. Though a priority was given to gaining more precious torque, when the lower amplitudes were checked with a frequency sweep test, no significant changes appeared in the results. The linear limit was checked at different temperatures, and gave the same limit, approximately.



Figure 3.9: Linear viscoelasticity limit of bio-hydraulic oil at 1Hz frequency

3.3.2 Time Dependency of the Elastic Modulus

Figure (3.10) summarizes the results of the multi-oscillation tests of different samples. The gaps and frequencies were 0.5mm and 1Hz, respectively. Beside bio-hydraulic oil, engine oil and silicone oil were tested for the purposes of comparison and validation. Only bio-hydraulic oil showed a growing G'. This change could be result of different activities, for example: drying, oxidation, accruing, or microstructural change. If any of these reactions take place, except microstructural change, the change will be permanent. This raises the question of whether or not the G' can be deconstructed and reconstructed again.



Figure 3.10: Time dependence of the dynamic shear modulus G' for different oils at 0°C

3.3.3 Frequency Sweep

A frequency sweep test was conducted on bio-hydraulic oil under a gap of 0.3mm. Figure (3.11) plots G' and G" with respect to frequency, and Figure (3.12) summarizes the relation between G' and temperature. The last experiments not only revealed the viscoelasticity of bio-hydraulic oil but also the solid-like behavior in which G' exceeds G" at low frequencies. G' hit its plateau region under the frequency of 1Hz.



Figure 3.11: Frequency sweep of bio-hydraulic oil at different temperatures



Figure 3.12: Storage modulus of bio-hydraulic oil at 1 Hz versus temperature

In other research, using SAOS on cholesteric liquid crystals with inclusions exhibited

similar behaviour [34]. Further, it was mentioned that it also exhibited the typical behavior of a Maxwell fluid at an angular frequency of more than 10 rad/s, while it showed clear features of gel-like behavior at a lower frequency. Comparably, we found that the Maxwell model can fit the bio-hydraulic oil at a temperature of $0^{\circ}C$ and at an angular frequency of more than 60 rad/s. Consequently, the relaxation time is 0.93 msec. The fitting of the Maxwell model is shown in Figure (3.13).



Figure 3.13: Maxwell model fits bio-hydraulic oil's result at 0°C

3.4 Low Shear Rate

After the nature of G' time dependency was recognized, it became necessary to check the viscosity against the shear rate again, this time at a very low shear rate, which allowed for enough time for to G' to grow. Figure (3.14) clearly shows the shear thinning behavior of the bio-hydraulic oil while temperatures are below 30°C. There was no tendency to reach the plateau viscosity at very low shear rate. This predicts the presence of yield
stress; meanwhile it strengthens the credibility of the frequency sweep results in the sense of exhibiting solid-like behavior at a low frequency.



Figure 3.14: Shear thinning behavior of bio-hydraulic oil

3.5 Gap Size Influence on Elastic Modulus

Gap size effect was investigated in the case of bio-hydraulic oil; the summarized results in figure (3.15) show a strong relevance to G'. While G' decreases with gap size, G" changes slightly. This confirms that the variation in G' cannot be due to the gap errors. G' reached either a peak or a constant value after a certain gap size. Even though this behavior was predicted more by the curve fitting, it is more obvious in the case of the bio-chainsaw oil (figure (3.16)),where, the change was sharper. In an effort to explain this phenomenon, we assume two scenarios and the third is a combination of the first two. The first assumption is that the structure of bio-oil is relatively large with respect to gap sizes of less than 0.6mm. The second scenario is that the bio-oil's structure is affected by its contact with the geometry surface, and this effect becomes more obvious when the gap becomes narrower. In the literature, gap size effect was investigated on a Nano scale base in the case of n-hexadecane [82].



Figure 3.15: Effect of gap size on elastic and loos moduli, bio-hydraulic oil at $0\,^\circ\mathrm{C}$ and 1 Hz



Figure 3.16: Effect of gap size on shear moduli, bio-chainsaw oil at 0°C and 1 Hz

3.6 The Delicate Structure of Bio-hydraulic Oil

The previous results proved how the state of bio-oil is a function of temperature, time, and occupied space. In addition, it was affected by pre-shear. This is another sign of the presence of structure. This delicate structure can be built over time and deconstructed by shear. In order to demonstrate this behavior, a complex viscometery test was conducted. The test has three sequential procedures, which are explained in figure (3.17). The response to the input signal is presented in figure (3.18). The viscosity increased in a logarithmic manner as result of the first procedure, which involved a constant application of very low shear stress for 5 minutes. The second procedure was growing a shear ramp, and gave the expected shear thinning behavior. The third procedure, which was the same as the second in reverse growth, deviated in its result from the second one, which is a sign of hysteresis behavior. The three procedures draw a complete loop on the viscosityshear rate diagram. It is worth mentioning when the first procedure was repeated again,



Figure 3.17: The input signal of multi procedure experiment (3.18)

the viscosity followed the same path but at a much slower rate. The explanation for this comes from the sample history. Whereas the first procedure was preceded by a test under the linear limit, the fourth procedure was preceded by procedure 3, which exceeded the linear limit.

3.7 Structure Recovery of Bio-hydraulic Oil

The previous experiment demonstrated structure building and structure recovery. Considering G' is a more reflective property of the micro structure of the oil, it is meaningful to use G' to test structure recovery. As explained in the literature [77], the SAOS was used to study structure recovery, crystallization, and accruing [36]. This test consists of three procedures, which are single frequency oscillation tests. While the first and the last were performed under linear limits, the second had a substantially larger amplitude than the linear limited tests. The purpose of organizing the tests in this way is to allow



Figure 3.18: Viscosity of bio-hydraulic oil due to sequential multi shear test

the structure to grow up; destroy the built structure; and, finally, observe the structure recovery in the last procedure. The structure recovery has important impacts on certain applications, such as inking [77]. In the case of lubrication, the impact of structure has never been studied. An experiment was conducted twice on the bio-hydraulic oil, at 0.4 mm and 0.2 mm gaps. The frequency was 1Hz. The oscillation amplitudes were 10%, 500%, and 10%. The results are presented in figures (3.19, 3.20) and summarized in table (3.2).

ave	rage growing rate	Percentage of decrease in G' due	
Gap	First procedure	Third procedure	to over shearing oscillation
$0.2 \mathrm{~mm}$	0.0152	0.0155	27.2 %
0.4 mm	0.0171	0.0145	33.3 %

Table 3.2: Summery of structure recovery tests on bio-hydraulic oil

The G' growth after over-shearing followed almost the same pattern as in the first procedure. The decrease in G' varied from 27.2 to 33.3%. This gives an indication of

structure stability. However, we do not have a comparable case to estimate the strength of the structure. The larger gap was affected more; the Reynolds number was larger also. It is like a quick mixing of a Lego structure. It will be destroyed, but it will not likely return to single pieces, as it was originally. The sharp decreasing in G' that took place after 12 minutes is not a random behavior. It is a repeating phenomenon and shows up more clearly in the smaller gap.



Figure 3.19: Structure recovery of bio-hydraulic oil at 0.4 mm gap



Figure 3.20: Structure recovery of bio-hydraulic oil at 0.2mm gap

3.8 Rheometry as Technique to Study Surfactant Behavior

Based on the previously presented work, many indications have led to the conclusion that some surface activity between the oil and the geometries do affect the rheological behavior. The self-assembled monolayer is a nano-phenomenon. And while some nano tools are used to study it, such as analytical transmission electron microscopy (ATEM) and atomic force microscopy (AFM), some macro techniques are also used to measure this reaction, such as surface tension and Langmuir–Blodgett trough. Using a rheometer to study the surface activities is new.



Figure 3.21: Elastic modulus versus time at gap 0.2 mm and frequency 4Hz

3.8.1 Impact of Surface Conditions of the Geometry on Rheological Behavior

We aimed to demonstrate the effect of the self-assembled layer on the bulk properties of bio-lubricant. Single amplitude oscillation was used to observe the behavior of G'. The geometry was cleaned in the first experiment using the mentioned method, whereas it was only wiped out with a paper towel in the second experiment. The surface in the second experiment was clean apparently. We did not conduct any analysis to diagnose the surface chemical composition, but we assumed that the self-assembled layer-or part of it- stayed on the surface if it indeed existed. The result is reported in figure (3.21).

We first noted that the not-cleaned surface had a lower G' and a smoother curve. This supports the assumption that the increasing G' with respect to the gap size could be due to the elimination of the surface effect. The smother G' growth is a possible indication that the self-assembled layer was already developed and any reaction with bulk properties took place early. The sharp drop in the G' that we reported before appeared in this experiment also. Moreover, it happened again after three hours. If the two experiments, with clean and not clean geometry, would ultimately lead to the same regime, other drops in G' would be required to meet both curves.

3.8.2 Impact of Geometry's Material on Rheological Behavior

A further step was taken to investigate the effect of the surfactant behavior using SAOS. The geometry used was stainless steel made, but it was also covered by a sheet of plastic 0.17mm thick. The influence of the geometry material was measured, and figure (3.22) shows the results of four frequency sweep experiments at different gaps. Firstly, the sample was tested at a gap of 0.5mm, which was then squeezed to 0.2 mm and tested again. The systematic repeating effect of the contact surface material on the rheological behavior was identified in the results. In addition, the difference in G' due to using plastic and stainless steel geometry increased with decreasing the gap. (Note the difference between h1 and h2 on the graph). Once again, this supports the idea that one of the reasons behind G's gap size dependence comes from the reaction with the surface.

The above experiment was conducted again, but with 2% tetrafluoroborate added to the hydraulic oil. The added material, ionic liquid crystals (ILC), is a strong surfactant that have been used in previous researches as lubricity improvers. More details will come in chapter (5). The object of this experiment was to change the microstructure and surfactant nature of bio-hydraulic oil. Thus, if a change is observed in the bio-lubricant's behavior against geometry materials and gaps, it will confirm the last conclusion which is the effect of the surface extends and affects the bulk properties of the oil. It should be pointed out that the sample was replaced in order to check another gap size, instead of squeezing the larger gap, as before. Where squeezing the gap made a sharp change in the sample behavior, in contrast, the bio-hydraulic oil's G' did not show a significant



Figure 3.22: Frequency sweep test of bio-hydraulic oil at 0 $^\circ\mathrm{C},$ and with different geometry materials

difference between the squeezed or completely replaced sample. Remember that biohydraulic oil is a more homogenous material than the ILC solution. We doubt that the ILC concentrated beside the surfaces, so the squeezing changed the concentration of the sample.

Figure (3.23, 3.24) represents the results in the cases of replacing and squeezing the sample, respectively. The effect of the gap size and geometry materials is less important in this case. On the other hand, the change in behavior due to the gap change was more obvious, especially in the case of the stainless steel geometry. Meanwhile, the plateau region became unclear in the case of the 0.2 mm gap & stainless steel surface. We wonder if the ILC took, or competed with, the bio-oil settling on the surface. This would affect the boundary regime and how it interacted with bulk fluids. Interestingly, the effects of the additives not only appeared on the readings, but could also be seen in the samples after the test. Figure (3.25) shows pictures of the bio-hydraulic oil and the



Figure 3.23: Frequency sweep test of 2%ILC at 0°C with different geometry materials, the sample was replaced

2% ILC samples taken immediately after the geometry was lifted up.



Figure 3.25: Pictures of the samples after tests on the lower plate



Figure 3.24: Frequency sweep test of 2% ILC at 0° C; the sample was squeezed

3.9 Polarized Light Microscopy

According to the results, a number of consistent behaviors led to the idea that biolubricants behave like liquid crystals. One thing known about liquid crystals is their interesting interactions with light. In order to investigate this assumption more thoroughly, we used a polarized light microscope, Anton Paar brand, to examine our samples, which is shown in Figure (3.26). Compared with the emulsion of water in bio-oil, the bio lubricant did not act as a strong transitive to polarized light, though it showed interactions with light according to temperature and applied shear. Pictures of some seen events are reported in Figure (3.27).



Figure 3.26: Anton Paar, polarized light microscope



80% of mineral hydraulic oil plus bio oil at 10 s-1

Figure 3.27: Polarized light microscope pictures on Anton Paar rheometer

The gap was about 0.1 mm under a flat acrylic geometry. The heating rate was about 8°C/minute. Gap size and heating rate had not been studied. Many views through the polarized microscope support the assumption about liquid crystals. The following are

the most important notes:

- The bio-lubricant's interaction with polarized light depended on the temperature.
- The light activity stopped at temperatures under -15°C. This could be due to the oil starting to solidify, and any motion by molecules to align themselves became difficult.
- Changing the temperature without a shear did not change the state of the transmitted light, remembering that the heat rate was high. In contrast, a significant change took place when the change in the temperature was associated with shear. Possibly, the shear helped the molecules to move and align themselves.
- A temperature of about 40°C marked a changing point in the bio-oil's behavior also for polarized light microscopy, back to (2-2-1).
- A periodic change in colour was noted under the shear. While these changes increased with the shear, no clear borders between one color and another were noticed. However, the change in colour showed more contrast, which meant that borders were more easily identified in the mixture between mineral and bio-hydraulic oil of 80/20. In addition, the contrast in color not only appeared in a sequential periodic manner, but also showed up in separate objects similar to meteors. These are shown in figure (3.27).
- Some dark aggregates appeared in the mixture of bio-oil with cholesteryl chloride (LC). We could not see if they were in a crystalline phase or merely undissolved particles.

3.10 Liquid Crystal Additives

While it was decided that tribological experiments could evaluate the performance of the lubricant quantitatively, we needed something more than that to explain the mechanism of that performance. The results of tribological tests of two solutions of liquid crystals, with bio-hydraulic oil, will be given in chapter (5). The liquid crystal solutions are 2% tetrafluoroborate (2% ILC) and 10% cholostryl chloride (10% LC). The ultimate goal is to make a connection between their tribological and rheological behaviors. While viscoelasticity could give an indication of the microstructural nature of the lubricant, the viscoelasticity could give an indication of the reaction between the molecules of base oil and the additives. However, it is not clear what the relation between the microstructure and the lubricity is. This experiment is an effort to find this kind of connection. We used a single frequency oscillation test under a constant heating rate of 0.5°C/min. The test covers a temperature domain of between -5 to 100° C. Figures (3.28, 3.29) plot G" and G' versus temperature. In terms of G", both liquid crystal solutions affected the thermal stability of the viscosity, while they kept the same behaviour along most of the temperature domain. However, G" increased sharply at temperatures below 0°C, in the case of 2%ILC. By contrast, G' had different values in the case of 2%ILC, and showed a different pattern that was almost constant along the temperature domain. Neither the temperature rise nor the small shear amplitude was able to break the structure that occurred at the low temperatures, assumedly. LC lowered the G' and followed a similar pattern to that of the pure bio-hydraulic oil.



Figure 3.28: Oscillatory temperature sweep, loos modulus (G")



Figure 3.29: Oscillatory temperature sweep, elastic modulus (G')

3.11 High Pressure Rheology

Lubricating is usually associated with high pressure. While the pressure could exceed one MPa in the hydrodynamic regime, it could exceed one GPa in the boundary regime. High pressure causes increases in both the density and viscosity of oil .The used high pressure cell mounted on Anton Paar rheometer is shown in figure (3.30). The pressure cell has a capacity of 0.4 GPa, depending on the pressure of the supplied compressed gas. It is completely sealed, with a cylinder and cup inside, and the torque is transmitted via magnetic coupling. The compressed gases used were CO2 and N2, and the results of CO2 are presented in figure (3.31):



Figure 3.30: Anton Paar high pressure cell (reproduced image) [83]

It was found that the viscosity of bio-hydraulic oil was inversely proportional to the pressure when the compressed gas was CO2. Figure (3.31) is the relation between the viscosity and the pressure in the case of CO2. We believe that the absorbance of CO2 into the oil was responsible for the decrease in viscosity, which was extensively released after the pressure cell was opened, in a manner similar to boiling.



Figure 3.31: Viscosity of bio-hydraulic oil under pressure of CO2



Figure 3.32: Bio-hydraulic oil viscosity versus CO2 pressure drop, maximum pressure 3.6 MPa

No calibration was done to estimate the gas escaping from the cell, but the decreasing

viscosity with time confirms that the drop in the viscosity was due to the CO2 being absorbed. Figure (3.32) shows the relation between the viscosity and the pressure drop. Accordingly, it is difficult to decide the impact of the shear rate, where a higher shear rate could increase the mixing and exposure to the CO2. Decreasing viscosity with respect to CO2 pressure was reported in a study on corn oil and connected to the dissolution of CO2 [28]. In contrast, the viscosity increased with respect to the pressure when N2 was used instead. This is represented in figure (3.33), where the viscosity increased about 6% by increasing the pressure from 0.13 to 1 MPa.



Figure 3.33: Viscosity of bio-hydraulic oil under pressure of N2

3.12 Conclusions

While most of our effort were focused on bio-hydraulic oil, the experiments that were conducted on the three samples of bio-lubricant showed considerable similarity. The bio-lubricant has a constant viscosity at moderate and high shear rates. Accordingly, its similarity to Newtonian fluids is valid for most applications. In contrast, viscoelasticity was investigated using SAOS, and shear thinning was noted at a very low shear rate. It was found that the viscoelasticity of bio-oil is function of time, temperature, gap, and surfaces materials, which means revealing important information about its microstructure and surface activities. The experiments conducted consistently led in the direction of our assumption of its similarity to Liquid crystals. Further, something is formatting on the surface and decreasing the G'. Meanwhile, the self-assembled mono layer has an organized structure. Thus, if it extends in the direction of the fluid, the extended layers will be likely organized, too. The extended monolayer was reported before in some researches, but in nano level [82]. As a result, we are imagining two existing phases of liquid crystals at least; they compete with each other, as was shown in the gap size and geometry material effects in section (3.8). We expect that the boundary phase is Smectic while the bulk phase could be complex. This idea is illustrated in figure (3.34).



Figure 3.34: Imaginary simplified scenario of bio-hydraulic oil crystallization within a small gap

Chapter 4

Thermal Analysis

4.1 Overview

Thermal Analysis (TA) "means the analysis of a change in a sample property, which is related to an imposed temperature alteration. Calorimetry means the measurement of heat" [85]. Change in a sample could be due to a chemical reaction, biological activity, microstructure, or phase transition [86], which means that TA could reveal important information, for instance: specific heat, composition, oxidation and thermal stability, as well as different characteristic points that indicate glass transitions, melting, boiling, and crystallization. The main focus of this chapter is to connect rheological and thermal behavior, while also investigating the changes in microstructure. Some transition points were observed in the results, such as pour point. However, they will not be discussed in details because parallel experimental work is needed to be able to read on the TA curves correctly. Differential Scanning Calorimetry (DSC) is the TA technique that was used in this study. It involves measuring the heat flow with respect to temperature under the programmed heating rate. The heat flow is determined by the following equation:

$$\frac{dQ}{dt} = \beta C_p \tag{4.1}$$

Where Q is heat, t is time, β is heating rate Cp is heat capacity. The heat capacity is the only material property showing in the last equation.

4.2 Experimental Setup Apparatus

Figure (4.1) shows multi-cell differential scanning calorimeter, MC-DSC4100, which was used in this research. It is furnished with four ampoules which can host three different samples in the same experiment while the fourth works as a reference. The ampoules were made of stainless steel with screwed caps. MC-DSC 4100s can cover temperature ranges from -40 to 110 ^{o}C with a heating rate from 0.1to $2^{o}C/min$, and sensitivity 1 μ W [87].



Figure 4.1: The calorimeter used, MC-DSC4100

The heating rate for all the results presented here is $0.2 \ ^{o}C/\text{min}$. The temperature ranges from -30 up to 100 ^{o}C . Since the DSC experienced instability during start up, it was eliminated. The same experiments were done on empty ampoules, and any deviations from zero were subtracted from the results. The ampoule cleaning and sample preparation are detailed as follows:

<u>Ampoule cleaning</u>: The ampoules were rinsed and sonicated for 10 minutes with different solutions: detergent, nano-pure water, ethanol, nano-pure water twice, and finally, methanol. Then, they were left to dry in the ambient temperature before putting them in the oven at 80° C for 1 hour. The ampoules were weighed before filling, after

filling, and after the test, using a digital scale.

<u>Sample preparations:</u> All tested samples were degassed using a vacuum chamber. They were injected slowly at the lower surfaces of the ampoules using clean syringes.

4.3 Results

4.3.1 Repeatability and Reversibility

A heating-cooling-heating test on the bio-hydraulic oil was repeated twice; the first and second heating runs gave almost the same results, within a range of 0 to 100° C. Thus, no permanent change had taken place, and the microstructure of the oil was recoverable within the tested domain. Figure (4.2) shows the heating and cooling curve of the 0.56g of bio-hydraulic oil. While we expected the existence of a gap between the heating and cooling curve at a high heating rate, it decreased at the lower heating rate [88]. In other words, the lower heating rate gave the oil enough time to develop its structure. The curves overlapped from 10 to 50°C, and separated again after that. This predicts the existence of another peak at temperature above 100° C, assumedly. The cooling test started from 110°C, so this high temperature could affect the following lower temperature behavior on the cooling curve.

4.3.2 Sample Size

Ideally, the size of the sample should not influence the result, yet figure (4.3) reveals a relationship between the sample mass and ejected heat. This effect not only translated into different values, but also affected the pattern of the curves. While curves of 0.18g and 0.56 g keep in parallel, the curve of 0.05 g shows a different behavior. Based on our notes, this behavior was more likely real than merely the result of errors. The difference between curves 0.05 g and 0.18g becomes clearer at temperatures from 0 to 25° C. This



Figure 4.2: The DSC heating and cooling curves of bio-hydraulic oil

is the same range at which the bio-hydraulic oil has relatively high G' according to the rheology results. Curves for 0.05 g and 0.18 g correspond to each other at intervals lower than -13° C. This agrees with the polarized microscopy results in section (3.8). Curve 0.05 g has a form of arc that is tangential to curve 0.18g at around 45°C. The sharp drop around 71°C increased as the mass decreased. While smaller mass samples have smaller depths, the effects of walls will be larger. Assuming that the oil has a structure that could be initiated or stimulated by metal walls, this can explain the impact of sample size on DSC results.

4.3.3 Transition Points

Transition temperatures were located on the DSC heating curve of the 0.05 g sample (see Figure 3-4). While different points could show up on a cooling curve, they will not be discussed because they could be the same points under lagging. The used apparatus has a defect at around 20°C, so any event around that temperature cannot be taken



Figure 4.3: DSC cooling curves for different mass samples of bio-hydraulic oil

into account. The interesting thing about this curve is that the transition points were not associated with lower temperatures exclusively, but also occurred at relatively high temperatures, like 60°C. It was difficult to investigate G' at that region due to obvious practical difficulties. It was noted that the drop that happens at around $60^{\circ}C$ does not show up at a faster heating rate. This is understandable because it is a sharp event, and any faster heating rate will miss it. They could be two neighbouring drops, but the double drop appeared only on the small sample. A drop of around the same temperature was reported on the DSC of palmitic acid [36], and not far from it was measure in sediment that was extracted from canola oil [63].

A similar behavior was reported by a study on undatus seed oil [60]. The last reference reported such details on DSC transition points of bio-oil. Additionally, Endothermic heat flow continues to rise up, even at relatively high temperatures, similarly to what we measured. Consequently, it was seen as a good case to compare our results with. Table (4.1) lists transition points for different oils. In terms of chemical composition,



Figure 4.4: Transition points on heating the DSC curve of bio-hydraulic oil

undatus seed oil is not much different from canola oil. A comparison between both is found in table (4.2). In contrast, undatus oil has more than double the saturated fatty acids that canola oil has. Is this the reason behind the fact that the transition points in the undatus oil case are more distinguishable Finally, where the saturated fatty acids have greater tendencies to crystalize, oleic acid has the opposite [59].

Sample	Transition temperature on melting curve (°C)					
Sample	1	2	3	4	5	6
Canola oil	OOR	-20	-16.5	-	6.5	60
Undatus oil	-35.75	-25.39	-16.77	-5.64	5.46	OOR
Palmitic acid	OOR	OOR	OOR	OOR	OOR	62.7
Canola sediment	OOR	OOR	OOR	OOR	OOR	75.2 - 78.7

Table 4.1: Comparison transition points [58,61,34]

OOR: out of the range

Fatty acid	Canola oil	Undatus seed oil
Palmitic (C16:0)	3.68	12.78
Stearic (C18:0)	1.65	4.67
Oleic $(C18:1)$	63.49	24.43
Linoleic (C18:2)	20.05	55.63
Linolenic (C18:3)	9.46	1.18
Saturated fatty acid	7	17.99

Table 4.2: Comparison between chemical composition of canola oil and undatus [13, 14, 60]

4.3.4 Different Bio-lubricants

Besides bio-hydraulic oil, bio-gear oil and bio-chainsaw oil were scanned as well, and the results are reported in figure (4.5). The tested sample masses were 0.378g, 0.49 g, and 0.56g respectively. A connection between DSC and rheological behavior was found again. Bio-gear oil and bio-hydraulic oil had parallel curves, whereas the bio-chain saw oil deviated from them at very low temperatures. When comparing this with their rheological behavior, bio-chain oil showed different behaviors at low temperatures. The gap between bio-gear and bio- hydraulic could be narrower if they had the same mass.

4.3.5 Impact of Liquid Crystal Additives on DSC

As to the heating curve, Figure (4.6), the three samples behaved similarly. If the size of the sample mass is considered, bio-hydraulic oil could have larger absorbed heat. The sample masses of bio-hydraulic, 2%IL and 10%LC, are 0.56, 0.37, 0.37 g, respectively. The sharp change came in the cooling experiment, where the 2%ILC sample did not eject any heat energy, relatively. We neglected the possibility of the sample escaping due to evaporation or oxidation, as the ampoules were scaled after the test. Either a chemical reaction had occurred, or a strong structure that could be destroyed by a temperature change had taken place. However, it is difficult to confirm this big change without repeating the test several times. It should be pointed out that the same sample



Figure 4.5: DSC cooling curves of different bio-oil samples

was used in both the heating and cooling procedures.



Figure 4.7: DSC cooling curves of bio-hydraulic oil plus liquid crystal additives



Figure 4.6: DSC heating curves of bio-hydraulic oil plus liquid crystal additives

4.3.6 Comparing Between DSC and Rheological Behavior

Recalling the oscillatory temperature sweep (3.10), the G' curve from the SAOS is consistent to some extent with the heat curve from the DSC tests, as shown in figure (4.8). This increases the credibility of the results.



Figure 4.8: Comparing the SAOS and DSC tests on bio-hydraulic oil (The heat flow axis is in reverse order for the purposes of clarification)

4.4 Conclusion

The TA results agreed to an encouraging extent with the literature, as well as with the rheometery and microscopic results. Comparing the noted transition points with those in the literature could reveal the components that have the greatest effect on crystalization in bio-lubricants. The influence of the mass on the DSC curves could be taken as indicators of surface activities. And while the correspondence between DSC and SAOS was not strong, it was nevertheless considerable. Both the cooling and heating curves followed similar and close paths. A transition point at temperatures higher than 100°C was predicted based on the differences between the two curves.

Chapter 5

Tribology

5.1 Overview

The concept of friction regimes was introduced earlier in the introduction. For the sake of clarification and unification of the terminology for the reader, we present this short overview. 'Wear' is "the surface damage or removal of material from one or both of two solid surfaces in sliding, rolling or impact motion relative to one another" [89]. While any or all of several different mechanisms (adhesive, abrasive, impact, chemical and electric) could produce damage and material loss, the actions of two of them are illustrated below:

<u>Adhesive wear:</u> regardless of whether it is fluid or dry friction, this action takes place between nominally flat surfaces rubbing against each other. Under severe pressure, a fragment from one surface could adhere to another. While adhered fragments separated from their original surfaces, due to the shear action, try to stay connected to another surface, may separate from both and become wear particle. This process can reverse in the opposite direction. Meanwhile, this phenomenon causes motion resistance and loss of mass. Figure (5.1) illustrates it.

<u>Abrasive wear:</u> unlike the preceding one, this process is not exchangeable in both directions. as it was with precedent one. It takes place when a rough harder surface is rubbing against a softer surface, so the wear is accrued due to plastic deformation and fracture.



Figure 5.1: Schematic drawing demonstrating the adhesive friction mechanism

5.2 Compression Investigation of Bio-lubricant Lubricity

The four-ball test or extreme pressure test was chosen for the purpose of investigating the lubricity of bio-lubricants. The nature of the surfaces of the contacting balls allow for achieving very high pressure, which could cause what is known as a weld or seizure point. Moreover, the surface area generated from the wear is an important measurement of lubricant wear resistance. Getting different scars from every test makes it more credible, statistically. Besides, we tested mineral hydraulic oil for the sake of comparison. Since this commercial oil was designed to be degradable and environmentally safe, it likely had restrictions on the number of toxic and nondegradable additives it could contain. Thus, we cannot confirm that this product would perform the same as any conventional lubricant. Also, its viscosity index is lower than the bio-lubricants. However, its grade was chosen to make its viscosity close to bio-hydraulic oil as much as possible at the test temperature of 75 °C. Eventually, in terms of the purpose and the grade it is comparable to bio-hydraulic oil.

5.2.1 Apparatus

The machine we used was a Falex-6 multi specimen wear tester, figure (5.2). It has a pair of aligned shafts, the upper shaft being the rotating one. The lower one is free to move, and loaded by static weights via a lever. The torque is measured by a torque cell. The first three balls are clamped fixed in an oil cup that is placed on the lower shaft. The 4th ball is centered above the first three balls and rotating via the upper shaft. The temperature is controlled by electric resistance heater, and measured by a thermo couple.



Figure 5.2: Falex-6 (multi specimen wear tester)

5.2.2 Experimental Setup

Ball bearings of 12.7 mm were used. They were made of extra-polished steel E52100, with a hardness of HRC 64. They were cleaned with detergent and acetone in a sonication bath before they were rinsed and dried with compressed air. The oil cup was filed with oil up to 5mm above the balls. Then it was given enough time to reach a steady state temperature before starting the test. The test conditions were chosen to be in compliance with standard test: ASTM D 4172 – 94 (2010) [90] as summarized in table (5.1):

Ball		Applied load	Rotation speed	Tomporaturo	Tost time	
	Material	Diameter	Applied load	Rotation speed	remperature	
	Steel E-52100	$12.7 \mathrm{~mm}$	$391.5 \ { m N}$	1200 RPM	$75 \ ^oC$	1 hour

Table 5.1: Four-ball test conditions

5.2.3 Repeatability

The test on the commercial lubricant was repeated three times. The scars' diameters were measured twice in two perpendicular directions. Thus, eighteen measurements gave an average of 469.3 μ m, with a standard deviation of 8.4 and a variance of 13%. The results are summarized in Table (5.2).

Table 5.2: Summarized results of four-ball test

	Lubricant	Scar diameter	Average COF	Minimum COF	Maximum COF
1	Bio-hydraulic	$397 \mathrm{um}$	0.107	0.066	0.133
2	Mineral hydraulic	$469 \mathrm{um}$	0.165	0.090	0.180

5.2.4 Scars

The scars presented in figure (5.4) were pictured using an electron microscope, that shown in figure (5.3), and measured using an optical microscope.



Figure 5.3: Scanning Electron Microscope (SEM)

The average diameter of the bio-hydraulic oil scars was the smallest, 397 μ m, compared with those of the mineral oil, which were 469 μ m. In the case of the mineral oil, the balls scars were not only larger, but also relatively rougher, (see figure (5.4)). The bio-hydraulic oil scars appeared in well-defined circular shapes, even though the wear was concentrated in a narrow region in the middle of the scar. The balls contacting areas were formatted in the shape of a circle, even without any wear due to the elastic deformation [89, 93]. The contacting pressure was not uniformly distributed, but was governed by the following equation according to reference [93]:

$$p = p_o \left(1 - \frac{r^2}{r_o^2}\right)^{\frac{1}{2}} \tag{5.1}$$

Where p_o is the maximum presure in the center, r_o is the radius of contacting area, r is the radius where the pressure is calculated. Consequently, it was expected that the wear was concentrating in the centre and following the path of worn particles or motion. The scar was distinguished inside the circular area because it was smaller than the static deformation. Thus, in the case of the bio-hydraulic oil, the real scar could be much smaller than what was calculated based on the diameter.



Figure 5.4: Four-ball test scars captured using SEM

5.2.5 Coefficient of the Friction:

The friction coefficient was calculated based on the equation (5.2) [92], and the curves were plotted against time, as in figure (5.5)

$$\mu = 222.707 \frac{M}{N} \tag{5.2}$$

Where M is the measured torque, N is the applied normal force. The constant in the equation is a function of the dimensions and geometry setup of the four balls



Figure 5.5: Friction coefficient versus time for bio and mineral hydraulic oils

Commonly, the coefficient of the friction is divided into different distinguished areas due to the changes in mating conditions between the rubbing surfaces: run-in and steady state sliding. High asperities may be knocked off during start-up, which will increase the real contact area and mating surfaces. In addition, the thin upper surface could be worn out, or new surface formatted on. All of these scenarios could lead to an increase or decrease in the coefficient of the friction. This period is called the run-in period,
which is followed by plateau period. The plateau period is called steady state sliding. The friction coefficient could rise up again after the plateau period, due to the effects of roughening or worn particles. This could be followed by another plateau, which is known as an S curve, or it could end in failure [89].

In the mineral oil test, the run-in period continued for three minutes approximately, followed by the plateau region. After that, the curve started to rise up again as a result of the roughening or worn particles, as has been mentioned. In the case of the bio-hydraulic oil, there was no distinguishable run-in period until after almost 10 minutes. Even after the test was finished, a significant part of the contacting area was still not clearly scratched. Preserving the same conditions on the surface kept the friction coefficient at around the same value. Even after raising the friction coefficient, there was no significant increase in the contact area due to wear. Thus, it was not confirmed that the scar reached a stable level [93]; neither it showed clear tendency to increase. In reference [95], the wear rate had two constant values periods and a jump in between. The contact pressure had a fall instead, simultaneously. It might have been a good idea to give the test enough time until the friction is completely developed, but it was timed for 60 minutes to fall in line with the standard. The researches on friction generally and on wear tests specifically confirm a decrease in the friction coefficient, with respect to the real contact area. Reference [94] was dedicated to investigating this phenomenon, and the results agree with most of the papers cited in this chapter. It is worth emphasizing that friction coefficient of bio-hydraulic oil was lower than that of the mineral oil, although it had a smaller contact area. This indicates that the bio-lubricant has superior lubricity.

5.3 Liquid Crystals as Additives to Improve Lubricity

It was mentioned in the introduction that liquid crystals are a matter of state for some materials, which have a less ordered structure than the solid state, which gives the material distinctive properties. Because liquid crystals have good or superior lubricating properties, they can be used as additives to the oils.

5.3.1 Samples and Experimental Setup

5.3.1.1 Lubricants:

In order to investigate the effect of liquid crystal additives on the performance of biolubricant oil, three different samples were tested:

- 1. Bio-hydraulic oil.
- 2. Bio-hydraulic oil plus 10 % of cholesteryl chloride, (10%LC).
- 3. Bio-hydraulic oil plus 2 % of 1-butyl-3-methylpyridinium, tetrafluoroborate, (2%ILC).

The additives were selected based on their positive results with mineral oils. In addition, they were chosen because of their diverse properties and chemical compositions, in order to cover a wide range of study possibilities. Due to capital and time costs, we were unable to test only a small percentage of additives and increase it gradually. In case of one try, the percentage of additives was intended to be large enough to have a significant effect. Meanwhile, they were small enough to dissolve thoroughly in the oil.

5.3.1.2 Preparation of 10% of Cholesteryl Chloride:

The quantities were measured using a digital scale (10^{-4} g) , and a 1 ml ordinary syringe. The smallest quantity that could be added depended on the size of a drop, which was around 0.01 g. Thus, the components with smaller mass sizes additives was scaled first, and then the oil. Generally, the accuracy of scaling was more than 99%. The loss in mass due to evaporation or adhering to beaker walls was not calculated. The mixture was heated up to $95^{\circ}C$, using a temperature controlled hotplate. Meanwhile, it was mixed using a magnetic stirrer for one hour after reaching 90° C.

5.3.1.3 Preparation of 2 % of Tetrafluoroborate

The mixture's components were measured in the same way as detailed above, and mixed up without any heating.

Note: the prepared samples were used over several months. And, despite being shaken gently before use, no physical changes were observed by the naked eye.

5.3.1.4 Pair of Friction

Chrome steel 52100 balls of 6 mm in diameter were used for this test. The disks were sheets of mild steel (C10-18) in thicknesses of 2 mm. They were polished manually by different grades of abrasive paper and diamond paste. The whole process took about 1 hour, as measurement to achieved roughness. They were cleaned with detergent and hot water before being rinsed with ethanol. Finally, they were dried by flame.

5.3.1.5 Experimental Setup

The test conditions are summarized in table (5.3), which were decided based on three variables:

- 1. Achieving the maximum stress to ensure being in the friction boundary region.
- 2. Giving the test enough time to observe the developing.
- 3. Considering the capabilities of the apparatus.

Ball		Disk		
Material	Material Diameter		Diameter	
Chrome steel 6 mm		Mild steel	24 mm	
Normal force	Rotation speed	Velocity	Test time	Distance
35 N	60 RPM	$75.4 \ 10^{-3} \ { m m/s}$	5 hours	$1.36 \ 10^3 \ {\rm m}$

Table 5.3: Pin-on-disk test conditions

5.3.2 Apparatus



Figure 5.6: Pin-on-disk setup

We used the Nanovea brand of the pin-on-disk setup, as shown in figure (5.6). Normal force was applied using dead weights. The balanced state, zero position, was set up with the aid of a digital scale. The friction force was measured using a load cell. After being tested using dead weights from 1 to 20 N, it was found that the error followed a logarithmic function:

$$\varepsilon_f = 0.0862 ln(f) + 0.0986 \tag{5.3}$$

Where: ε_f is the error, and f is the actual measured force. That gave us about a 5% error at 5 N. Part of this error could be due to the swinging weights in the calibration process. The vertical displacement of the ball that gives an indication of the wear rate was measured by a linear variable differential transformer (LVDT). Compared with metric gauges, it had an accuracy of 2 microns. However, we could not confirm that

error came from the LVDT or the metric gauges. Also, we noticed that, during the first two revolutions, the LVDT's reading moved up to 20 microns. This initial deformation could be due to any elastic deformation or to the machine itself. Thus, it was subtracted based on two points: firstly, we wished to make the readings more reasonable compared with the final depth of the scar. Secondly, this jump in the readings was almost constant over all the tests. After all, this phenomenon was noticed by other researchers, too [91]. The temperature was measured using a thermocouple, type K, that was place on the upper surface of the ball and connected to a PC via a multi-meter. The thermocouple accuracy was tested using mercury and a digital thermometer.

5.3.3 Results

5.3.3.1 Temperature

Since the apparatus did not have temperature control, the tests were conducted at room temperature, $26^{\circ}C$. The temperature of the balls became stable around 29 °C for all the tests. It was noticed that the temperature of the ball was higher than the temperature of the oil within 1°C. Figure (5.7) shows the recorded temperature for three tests.



Figure 5.7: Temperature versus time for pin-on-disk tests

5.3.3.2 Test Quality

Figure (5.8) shows the variations in the friction coefficient and LVDT readings for the three samples at a revolution of 18×10^3 , which were located at the end of the tests. All the samples had consistent values at different angles, which supports the credibility of the tests' results, statistically. In terms of material homogeneity and tested sample topography, we consider this graph as an indication of the test quality, especially in the absence of repeating the test several times.



Figure 5.8: Distribution of the friction coefficient and LVDT readings around the circular path at the revolution 18×10^3 .

5.3.3.3 Wear

LVDT readings are plotted in figure (5.9). The wear in both bio-hydraulic and 2% ILC oils had four stages: growing up, plateau, growing up, and finally another plateau. Alternatively, this is called an S curve [89]. In the case of the 10% LC, the wear continued until it finally approached a steady state. This agrees with reference [95], where the wear almost stops after the scar reaches critical size. The profiles of the final scars on the disks were measured using the LVDT at four positions around the path. These measurements are reported in table (5.4) and figure (5.10). Even though the reading of the LVDT at the end of the test was almost double the final depth for the bio-hydraulic oil specifically. all the scars were in the same depth approximately.

Lubricant		Max Depth of the scar		Cross-section area of the scar		Total woar
	Dublicant	Average	Variance %	Average	Variance %	10tai wear
1	Bio-hydraulic	$27.4 \mathrm{~um}$	17.0%	$0.0147 \ mm^2$	12.0%	$0.555 \ mm^{3}$
2	10% LC	$27.23~\mathrm{um}$	9.9%	$0.0165 \ mm^2$	10.0%	$0.623 \ mm^3$
3	2% ILC	30.9 um	19.0%	$0.0146 mm^2$	29.7%	$0.553 \ mm^3$



Figure 5.9: LVDT reading versus distance for 5 hours

The maximum average wear on disks was obtained in the 10% LC case, and the smallest was in the 2% ILC case. In contrast, the depth came in the opposite order. The complexity of the tests requires more care in examining the results. Where the balls had harder materials than the disks and the wear on them changed the contact area, the wear could continue on the disks without changing the contact area and pressure, significantly. Thus, it is more reasonable to consider the size of the scars on the balls as a good measurement of lubricity. The balls and disks were examined again under dissecting and a digital microscope, (See figure (5.11)). The wear on the balls took different patterns, which are schematically drawn in figure (5.12). The wear in the cases of the 2% ILC and 10% LC distributed around the sides, so the balls did not lose much from their original heights, whereas in the bio-hydraulic oil case, the wear took place on the tip. This explains the reason behind the difference between the LVDT readings and the depths of the final scar. It was noted that the wear on bio-hydraulic ball was the roughest. Measuring the width of the scars using the LVDT or microscope images gave different values. There is an inclination to consider the largest value, which came from the microscope image, because it validates the assumption that the depth of the scar is inversely proportional to its width for all oils.



Figure 5.10: Profiles of the scars on the disks



Figure 5.11: Dissecting microscope and digital microscope

The largest scar on a ball was in the case of the bio-hydraulic oil, while the smallest was in the case of the 2% ILC. Considering the profile of the scars on the disk, the 10% LC lost the largest volume while the 2% ILC lost the least



Figure 5.12: Pin-on-disk scars, a) schematic drawing for the matching between ball and disk; b) scar on ball, c) ball and disk; d) scar on disk

5.3.3.4 Coefficient of the Friction

The friction coefficient was plotted against the sliding distance for the three samples in figure (5.13), and the values are summarized in table (5.5). All the samples showed defined run-in periods. And, as to the four-ball tests, there is a comfortable agreement between them. The second half of the bio-hydraulic oil curve had more important variations. Considering the scars, the bio-hydraulic oil had the roughest surface also. Significantly, however, the bio-hydraulic oil still had the lowest friction coefficient. The 2% ILC had the most stable curve, which is an indication of keeping the same conditions of friction. In the case of the 10 % LC, there was a continuous decrease in the friction coefficient. Back to LVDT curve, it also behaved in an almost stable manner, in terms



of the wear. Thus, the continuing wear or increasing contact area could be responsible for this behavior.

Figure 5.13: Friction coefficient Versus time, Pin-on-disk tests

	Lubricant	Minimum COF	Maximum COF	Average COF
1	Bio-hydraulic	0.052	0.095	0.072
2	10% LC	0.132	0.169	0.153
3	2% ILC	0.104	0.133	0.123

Table 5.5: Friction coefficient for pin-on-disk tests

5.4 Conclusion

The ionic liquid crystals improved the wear resistance property of the oil, while the friction went higher. This needs to be investigated further, with more stable and identical contact areas, such as with a washer on disk setup. In addition, the effect of temperature, the percentage of the additives, and the type of rubbing coupling deserve to be investigated. The 10 % LC did not have a positive impact on the oil. Although, it is known from the literature that it has good surfactant properties, especially with steel. This raised many questions about its compatibility and competitivity with bio-oil molecules. Recalling from the rheology characterization (3.8, 3.10), adding cholesteryl chloride to bio-hydraulic oil decreased the G' prime slightly, which could be interpreted as showing that its molecules were not incompatible with bio-hydraulic oil molecules. In addition, the investigation into the surfactant behavior of 2%ILC showed less influence on the bulk properties, which could be interpreted as showing that the bio-hydraulic oil had a thicker boundary regime.

Chapter 6

Conclusion and Future Work

6.1 Achievements

To our awareness, the presented research is the most extended study on the rheological characterization of low viscosity bio-lubricants. This is the first study to investigate the effects of the geometry material on the rheological response of the tested material, as well as to present rheometry and thermal analyses as techniques for studying the surface activities. More credible equations to fit the viscosities versus temperature were proposed. Using the rotary rheometer to apply a broad shear rate range on low viscosity fluids was demonstrated. Furthermore, the viscoelastic and liquid crystal nature of the bio-lubricants were revealed. Excellent lubricity of bio-lubricant, and the impacts of liquid crystal additives on it were investigated.

6.2 Hypotheses

First hypothesis: The tested bio-lubricants behave like liquid crystals.

Argument:

- It has a significant elastic modulus (G') even the molecular weight it is not that large
- G' grows with time.

- G' is decayed by heating and shearing.
- G' with respect to angular frequency and viscosity with respect to shear rate. behave in similar manner to a cholesteric liquid crystal
- The polarized light microscope revealed optical activities according to changes in temperature and shear rate.
- Compared with mineral oil, canola oil has larger molecules that are highly polar.
- Crystalization or sedimentation are known phenomena in raw canola oil.
- The thermal analysis showed more events rather than melting and boiling points, and some of them at relatively high temperatures.

Discussion: The viscoelasticity of tested bio-oil cannot be due to the molecular structure only; it is smaller than that. Also, the growing G' cannot be due to oxidation, evaporation, or any other chemical reaction, because it is recoverable. To see the structure of the oil requires a microscope with enough magnification and suitable conditions to allow the crystals to grow. However, we expect the existence of more than one phase, which makes the case more complex.

Second hypothesis: The extended Self Assembled Monolyayer (SAM) into the bio-oil has a thickness much larger than the molecular length of a few nanometers.

Argument:

- The extended SAM affected the bulk properties
- There was a significant difference in G' between a 0.4mm gap and a 0.2mm gap, which means that the dimensions on such a scale make a difference.

Discussion: It is known that materials that have surface activity affect the surface tension [96], surface tension could affect the rheometry results. However, what happened in the bio-oil is more than surface tension, as the geometry surface that was in contact with the oil gave different results than the surface that was cleaned thoroughly.

Third hypothesis: the substrate material affects the microstructure of the bio-lubricant .

Argument:

- Geometry material affected G'.
- The effect of geometry materials maximized at narrow gaps.
- Adding ILC to bio-hydraulic oil diminished the effects of the subtrate.

Discussion: Previous results indicated a reaction between the surface and the biohydraulic oil. The ILC is a strong surfactant, therefore we suspect that it occupied the bio-hydraulic oil place on the surface. The self-assembled mono layer did not extend this time, so the effect of the gap was diminished. Even though the wear resistance was improved by adding ILC, the pure bio-hydraulic oil kept the lowest friction factor. The assumption of an extended self-assembled mono layer could explain that. In other words, while the ILC produced a stronger SAM , the pure bio-hydraulic oil had a much thicker one. Fourth hypothesis: The surfactant behavior could be studied using rheometry and TA

Argument:

- In rheometry, a type of coupling between the tested material and the geometry material affected the results, which we attributed to the surface activity.
- The SAOS result with carefully cleaned geometry differed from the result with reused geometry that only wiped out by paper towel.
- In TA, the more surface area with respect to the mass changed the behavior.

Discussion: The relative exposed surface area of the samples in DSC ampoules to the air and metallic walls increased with a decrease in the mass sample. However, the effect cannot be due to the reaction with air because it happened at both low and high temperatures; it maximized in some areas, and became ineffective in others. Using rheometry to study the surface activity will have an advantage in the field of lubrication, due to control of the testing conditions such as temperature, shear, and the posibility to apply an electric field or UV exposition.

Fifth hypothesis: the bio-oil has superior lubricity to the mineral oil.

Argument:

- According to the Four-ball test, the scar made with presence of bio-hydraulic oil was 15% less than that scare with presence of mineral hydraulic oil.
- According to the Four-ball test, the coefficient of friction of the bio-hydraulic oil is 35% less than that of the mineral hydraulic oil.

Discussion: The real scar produced by the four-ball test with the bio-hydraulic oil could be much less if it was took into account only the area where the erosion was concentrated .However, the coefficient of friction in the case of the bio-hydraulic oil was still the lower. This confirms the superior lubricity of bio-hydraulic oil over mineral oil.

Sixth hypothesis: Ionic liquid crystals (ILC)improved the lubricity resistance of bio-oil.

Argument:

- According to the pin-on-disk tests, 2% of the ILCs decreased the wear on the ball, the size of the scar on the disk and the worn volume from the disk.
- The sample that had 2% ILC had the most stable coefficient of friction based on the pin-on-disk test.

Discussion: It is not clear why the ILC improved the wear resistance, but the pure bio-hydraulic oil kept the lowest coefficient of friction. According to the rheological characterization work, we can assume that the ILC provided a stronger and faster formatted SAM. Still the pure bio-lubricant had a thicker layer. Further investigation into the effects of the normal force and time could confirm or invalidate this assumption.

6.3 Questions Raised

- If the bio-lubricant has different crystalline phases according to temperature, what is the tribological performance of each crystalline phase?
- If the bio-lubricant has different crystalline phases at the same temperature, how can they be studied separately?

- If the SAM of a bio-lubricant takes time to build up, how is this reflected in the tribological performance?
- If the crystalline behavior comes from different combinations in the bio-lubricant, what is the influence of every component on the tribological performance?

6.4 Conclusion

- A rotary rheometer can be used to perform SAOS and wide abroad shear tests on low viscous liquids under proper setups.
- Compared with tested mineral hydraulic oil, tested bio-lubricants had more stable viscosities over temperature.
- A double exponential equation can represent the changes in the viscosity against the temperature, accurately, under the tested domain.
- The yield stress in the bio-chain oil was measured in temperatures lower than 20 °C. The effect of temperature history faded by time.
- The bio-hydraulic oil has a characteristic curve (G' vs. frequency) similar to a cholesteric liquid crystals. G' has a plateau region under 1 Hz and intersected with G" at a lower frequency, which is an indication of solid like behavior.
- Bio-hydraulic G' time dependence was investigated. In contrast, engine oil did not show any time dependence.
- Gap size affected the rheological behavior of bio-lubricants.
- The surface activities of bio-hydraulic oil affected the rheometry results.

- The G' of bio-hydraulic oil, which indicates the microstructure, was decayed by shear and recovered by time.
- Compressed CO2 decreased the viscosity of bio-hydraulic oil while compressed N2 increased it under the tested range of tested pressures.
- Some optical activities of bio-lubricants, according to shear and temperature changes, were able to be observed using a polarized microscope.
- Some transition points were noted on the DSC curves of the bio-lubricants which could denote crystallization, or represent signatures of certain compositions in the bio-lubricant.
- A correlation between the DSC and SAOS results was noted.
- The mass size affected the DSC results and denoted to the surface activities
- Bio-hydraulic oil exhibited better tribology performance when compared with tested mineral hydraulic oil, according to the four-ball test.
- According to the pin-on-disk test, and under the applied conditions, adding 2% of the tested ILC improved the wear resistance property of the bio-hydraulic oil, while the pure bio-lubricant kept the lowest coefficient of friction.

6.5 Future Work

6.5.1 Rheometer

The rheometer has advanced control software, very sensitive sensors, and very good control on the test conditions. It could be modified and improved to become an advanced general testing station. (rheometer, nano-tribometer, tensiometer, microscopy rheometer)

- We were limited in our ability to characterize diluted and low viscous solutions. Improving the methodology will reflect positively in the results. Further development of the geometries used to address specific applications is still needed. Some specific-use geometries are already in use, such as: multi wall cone, and plate and cylinder and cup.
- Use some alternatives to an electric motor to perform high frequency motions, such as the piezoelectric cell [97]
- As expected, using a polarized light microscope with high capabilities will allow observing the crystalline phases more closely. An ordinary converted microscope could be attached to the rheometer, GEMINI brand [98, 99].
- With change in design of the geometry the rheometer can be used as nanotribometer in order to get more precise measurements on the friction[100].
- Surface tension is a meaningful indication when studying surface activities; it is not difficult to use the rheometer as a tensiometer and get the benefit of its precise control.

6.5.2 Tribometer

A number of instruments and facilities can be added to the tribometer to enhance its performance and capabilities.

- A commercial circulating bath can be used to control test temperatures on the tribometer
- Using a pneumatic or electric actuator to apply normal force instead of dead weights, and using air bearings for the rotating table will reduce the vibrations.

- Using a micro ohmmeter to measure the electric resistance between the ball and the disk will help us understand the development of SAM and the contact area.
- Installing a digital microscope to observe the scar on the disk will help to observe it over time.

6.5.3 Mathematical Model

There is a need to improve the mathematical model, specifically for the lubrication problems; this can be done either by validating and modifying known viscoelastic and liquid crystal constitutive equations, or using Molecular dynamics to simulate the lubricating problem, especially within micro and Nano gaps.

6.5.4 Experiments

Endless numbers of experiments can be done to answer the questions were raised, understand the bio-lubricant better, and to develop and optimize new products. Furthermore, formatted SAM on the surfaces can be examined using X ray microscopy or atomic force microscopy. Different couplings of lubricants and rubbing surfaces under a matrix of conditions could be tested. Testing the same mass samples of bio-lubricant with different contact areas (oil/metal) in the DSC will confirm the measurements of the surface activity using thermal analysis.

Bibliography

- Greenland Corporation Environmentally Safe Lubricants [WWW Document], n.d. . URL http://www.greenpluslubes.com
- [2] Carrión, F.-J., Martínez-Nicolás, G., Iglesias, P., Sanes, J., Bermúdez, M.-D., 2009. Liquid Crystals in Tribology. International Journal of Molecular Sciences 10, 4102–4115.
- [3] Mang, T., Dresel, W., 2006. Lubricants and lubrication. Wiley-VCH; John Wiley [distributor]], Weinheim; Chichester.
- [4] Lubricants, US Industry Study with Forecasts for 2014 & 2019 (No. 2677), 2010.
 . The Freedonia Group.
- [5] World Lubricants, Industry Study with Forecasts for 2012 & 2017 (No. Study #2384), 2008. The Freedonia Group.
- [6] Baderna, D., Boriani, E., Giovanna, F.D., Benfenati, E., 2011. Lubricants and Additives: A Point of View, in: Bilitewski, B., Darbra, R.M., Barceló, D. (Eds.), Global Risk-Based Management of Chemical Additives I. Springer Berlin Heidelberg, Berlin, Heidelberg, pp. 109–132.
- [7] Bremmer, B.J., Plonsker, L., 2008. BIO-BASED LUBRICANTS, A Market Opportunity Study Update. United Soyabean Board.

- [8] D02 Committee, 2001. Test Method for Determining the Aerobic, Aquatic Biodegradability of Lubricants or Lubricant Components in a Closed Respirometer. ASTM International.
- CCOHS: Canada's National Centre for Occupational Health and Safety information [WWW Document], 2012. URL http://www.ccohs.ca/
- [10] Shahidi, F., 1990. Canola and rapeseed: production, chemistry, nutrition, and processing technology. Van Nostrand Reinhold, New York.
- [11] Canola Council of Canada Canola Council of Canada [WWW Document], 2012.
 . URL http://www.canolacouncil.org/
- [12] Chen, D., Tracy, N.I., Crunkleton, D.W., Price, G.L., 2010. Comparison of canola oil conversion over MFI, BEA, and FAU. Applied Catalysis A: General 384, 206–212.
- [13] Azian, M.N., Mustafa Kamal, A.A., Panau, F., Ten, W.K., 2001. Viscosity estimation of triacylglycerols and of some vegetable oils, based on their triacylglycerol composition. Journal of the American Oil Chemists' Society 78, 1001–1005.
- [14] Erhan, S.Z., Adhvaryu, A., Sharma, B.K., 2005. Chapter 22. Chemically Functionalized Vegetable Oils, in: Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology.
- [15] Erhan, S., Rudnick, L., 2005. Natural Oils as Lubricants, in: Rudnick, L. (Ed.), Synthetics, Mineral Oils, and Bio-Based Lubricants. CRC Press.
- [16] Bloch, H.P., 2000. Practical lubrication for industrial facilities. Fairmont Press, Lilburn, Ga.

- [17] Cheng, H., Hu, Y., 2012. Influence of chain ordering on frictional properties of self-assembled monolayers (SAMs) in nano-lubrication. Advances in Colloid and Interface Science 171-172, 53-65.
- [18] Rudnick, L.R., 2009. Lubricant additives chemistry and applications. CRC Press, Boca Raton, FL.
- [19] Hamrock, B.J., Schmid, S.R., Jacobson, B.O., 2004. Fundamentals of fluid film lubrication. Marcel Dekker, New York.
- [20] Rhodes, B., 2005. Vegetable Oil Based Internal Combustion Engine Oil, in: Rudnick, L. (Ed.), Synthetics, Mineral Oils, and Bio-Based Lubricants. CRC Press.
- [21] Sahoo, R.R., Biswas, S.K., 2009. Frictional response of fatty acids on steel. Journal of Colloid and Interface Science 333, 707–718.
- [22] Collings, P.J., 2002. Liquid crystals: nature's delicate phase of matter. Princeton University Press, Princeton, N.J.
- [23] Kai Liu. Viscoelastic flows within eccentric rotating cylinders journal bearings. A thesis submitted in partial fulfillment of the requirements for the degree of master of applied science in the University of British Columbia (Vancouver) October 2008
 © Kai Liu, 2008.
- [24] Wan Nik, W.B., Ani, F.N., Masjuki, H.H., Eng Giap, S.G., 2005. Rheology of bioedible oils according to several rheological models and its potential as hydraulic fluid. Industrial Crops and Products 22, 249–255.
- [25] Geller, D.P., Goodrum, J.W., 2000. Rheology of vegetable oil analogs and triglycerides. Journal of the American Oil Chemists' Society 77, 111–114.

- [26] Rabelo, J., Batista, E., Cavaleri, F. vio W., Meirelles, A.J.A., 2000. Viscosity prediction for fatty systems. Journal of the American Oil Chemists' Society 77, 1255–1262.
- [27] Quinchia, L.A., Delgado, M.A., Franco, J.M., Spikes, H.A., Gallegos, C., 2012. Low-temperature flow behaviour of vegetable oil-based lubricants. Industrial Crops and Products 37, 383–388.
- [28] Seifried, B., Temelli, F., 2011. Viscosity and rheological behaviour of carbon dioxide-expanded fish oil triglycerides: Measurement and modeling. The Journal of Supercritical Fluids 59, 27–35.
- [29] Chen-Ching Ting, Chien-Chih Chen, Viscosity and working efficiency analysis of soybean oil based bio-lubricants, Measurement, Volume 44, Issue 8, October 2011, Pages 1337-1341, ISSN 0263-2241, 10.1016/j. measurement. 2011.04.005.
- [30] Bengoechea, C., Cordobés, F., Guerrero, A., 2006. Rheology and microstructure of gluten and soya-based o/w emulsions. Rheologica Acta 46, 13–21.
- [31] S.K. Yeong, P.F. Luckham, Th.F. Tadros, Steady flow and viscoelastic properties of lubricating grease containing various thickener concentrations, Journal of Colloid and Interface Science, Volume 274, Issue 1, 1 June 2004, Pages 285-293
- [32] Wright, A.J., Marangoni, A.G., 2006. Formation, structure, and rheological properties of ricinelaidic acid-vegetable oil organogels. Journal of the American Oil Chemists' Society 83, 497–503.
- [33] Choi, H.J., Lim, S.T., Izumisawa, S., Jhon, M.S., 2005a. Viscoelasticity and solution viscosity of perfluoropolyether lubricants. Tribology International 38, 682–686.
- [34] Ramos, L., Zapotocky, M., Lubensky, T., Weitz, D., 2002. Rheology of defect networks in cholesteric liquid crystals. Physical Review E 66.

- [35] Hinkle, A., Shin, E., Liberatore, M., Herring, A., Batzle, M., 2008. Correlating the chemical and physical properties of a set of heavy oils from around the world. Fuel 87, 3065–3070.
- [36] Thareja, P., Street, C.B., Wagner, N.J., Vethamuthu, M.S., Hermanson, K.D., Ananthapadmanabhan, K.P., 2011. Development of an in situ rheological method to characterize fatty acid crystallization in complex fluids. Colloids and Surfaces A: Physicochemical and Engineering Aspects 388, 12–20.
- [37] Elsharkawy, A., 2000. Wax deposition from Middle East crudes. Fuel 79, 1047–1055.
- [38] Webber, R.M., 1999. Low temperature rheology of lubricating mineral oils: Effects of cooling rate and wax crystallization on flow properties of base oils. Journal of Rheology 43, 911.
- [39] Bair, S., Jarzynski, J., Winer, W.O., 2001. The temperature, pressure and time dependence of lubricant viscosity. Tribology International 34, 461–468.
- [40] Habchi, W., Vergne, P., Bair, S., Andersson, O., Eyheramendy, D., Morales-Espejel, G.E., 2010. Influence of pressure and temperature dependence of thermal properties of a lubricant on the behaviour of circular TEHD contacts. Tribology International 43, 1842–1850.
- [41] Binding, D., Couch, M., Walters, K., 1999. The rheology of multigrade oils at elevated pressures. Journal of Non-Newtonian Fluid Mechanics 87, 155–164.
- [42] Coy, R.C., 1998. Practical applications of lubrication models in engines. Tribology International 31, 563-571.

- [43] Williamson, B.., Walters, K., Bates, T.., Coy, R.., Milton, A.., 1997. The viscoelastic properties of multigrade oils and their effect on journal-bearing characteristics. Journal of Non-Newtonian Fluid Mechanics 73, 115–126.
- [44] Berker, A., Bouldin, M.G., Kleis, S.J., VanArsdale, W.E., 1995. Effect of polymer on flow in journal bearings. Journal of Non-Newtonian Fluid Mechanics 56, 333-347.
- [45] Davies, G.A., Stokes, J.R., 2008. Thin film and high shear rheology of multiphase complex fluids. Journal of Non-Newtonian Fluid Mechanics 148, 73–87.
- [46] Davies, G.A., Stokes, J.R., 2005a. On the gap error in parallel plate rheometry that arises from the presence of air when zeroing the gap. Journal of Rheology 49, 919.
- [47] Hughes, J.P., Davies, J.M., Jones, T.E.R., 1998. Concentric cylinder end effects and fluid inertia effects in controlled stress rheometry: part I: numerical simulation. Journal of Non-Newtonian Fluid Mechanics 77, 79–101.
- [48] James, P.W., Jones, T.E.R., Hughes, J.P., 2004. The determination of apparent viscosity using a wide gap, double concentric cylinder. Journal of Non-Newtonian Fluid Mechanics 124, 33-41.
- [49] Jones, T.E.R., Davies, J.M., Thomas, A., 1987. Fluid inertia effects on a Controlled Stress Rheometer in its oscillatory mode. Rheologica Acta 26, 14–19.
- [50] Andablo-Reyes, E., Vicente, J. de, Hidalgo-Alvarez, R., 2011. On the nonparallelism effect in thin film plate-plate rheometry. Journal of Rheology 55, 981.
- [51] Aly Franck. Measuring structure of low viscosity fluids in oscillation using rheometers with and without a separate torque transducer. ANNUAL TRANSACTIONS OF THE NORDIC RHEOLOGY SOCIETY, VOL. 11, 2003

- [52] Baravian, C., Benbelkacem, G., Caton, F., 2006. Unsteady rheometry: can we characterize weak gels with a controlled stress rheometer? Rheologica Acta 46, 577–581.
- [53] Remmelt Pit, Hubert Hervet and Liliane Leger. Friction and slip of a simple liquid at a solid surface. Tribology Letters 7 (1999) 147–152 147
- [54] Grecov, D., Clermont, J.-R., 2008. Numerical simulations of non-stationary flows of non-Newtonian fluids between concentric and eccentric cylinders by stream-tube method and domain decomposition. Rheologica Acta 47, 609–620.
- [55] Gwynllyw, D.R., Phillips, T.N., 2008. The influence of Oldroyd-B and PTT lubricants on moving journal bearing systems. Journal of Non-Newtonian Fluid Mechanics 150, 196–210.
- [56] Boucherit, H., Lahmar, M., Bou-Saïd, B., Tichy, J., 2010. Comparison of Non-Newtonian Constitutive Laws in Hydrodynamic Lubrication. Tribology Letters 40, 49–57.
- [57] Castillo-Tejas, J., Alvarado, J.F.J., Carro, S., Pérez-Villaseñor, F., Bautista, F., Manero, O., 2011. Rheology of wormlike micelles from non-equilibrium molecular dynamics. Journal of Non-Newtonian Fluid Mechanics 166, 194–207.
- [58] Adhvaryu, A., Erhan, S., Perez, J., 2002. Wax appearance temperatures of vegetable oils determined by differential scanning calorimetry: effect of triacylglycerol structure and its modification. Thermochimica Acta 395, 191–200.
- [59] Bell, A., Gordon, M.H., Jirasubkunakorn, W., Smith, K.W., 2007. Effects of composition on fat rheology and crystallisation. Food Chemistry 101, 799–805.

- [60] Lim, H.K., Tan, C.P., Karim, R., Ariffin, A.A., Bakar, J., 2010. Chemical composition and DSC thermal properties of two species of Hylocereus cacti seed oil: Hylocereus undatus and Hylocereus polyrhizus. Food Chemistry 119, 1326–1331.
- [61] Erhan, S.Z., Sharma, B.K., Perez, J.M., 2006. Oxidation and low temperature stability of vegetable oil-based lubricants. Industrial Crops and Products 24, 292–299.
- [62] Litwinienko, G., Kasprzycka-Guttman, T., 1998. A DSC study on thermoxidation kinetics of mustard oil. Thermochimica Acta 319, 185–191.
- [63] Liu, H., Biliaderis, C.G., Przybylski, R., Eskin, N.A.M., 1995. Physical behaviour and composition of low- and high-melting fractions of sediment in canola oil. Food Chemistry 53, 35–41.
- [64] Quinchia, L.A., Delgado, M.A., Franco, J.M., Spikes, H.A., Gallegos, C., 2012.
 Low-temperature flow behaviour of vegetable oil-based lubricants. Industrial Crops and Products 37, 383–388.
- [65] Tomšič, M., Prossnigg, F., Glatter, O., 2008. A thermoreversible double gel: Characterization of a methylcellulose and x-carrageenan mixed system in water by SAXS, DSC and rheology. Journal of Colloid and Interface Science 322, 41–50.
- [66] Masjuki, H., Maleque, M., Kubo, A., Nonaka, T., 1999. Palm oil and mineral oil based lubricants—their tribological and emission performance. Tribology International 32, 305–314.
- [67] Jayadas, N.H., Prabhakaran Nair, K., G, A., 2007. Tribological evaluation of coconut oil as an environment-friendly lubricant. Tribology International 40, 350–354.
- [68] Sahoo, R.R., Biswas, S.K., 2009. Frictional response of fatty acids on steel. Journal of Colloid and Interface Science 333, 707–718.

- [69] Sulek, M.W., Wasilewski, T., 2006. Tribological properties of aqueous solutions of alkyl polyglucosides. Wear 260, 193–204.
- [70] Latyshev, V.N., Novikov, V.V., Syrbu, S.A., Kolbashov, M.A., 2010. Tribological properties of some cholesterical liquid-crystal additives. Journal of Friction and Wear 30, 411–414.
- [71] Bermúdez, M.-D., Martínez-Nicolás, G., Carrión-Vilches, F.-J., 1997. Tribological properties of liquid crystals as lubricant additives. Wear 212, 188–194.
- [72] Amann, T., Kailer, A., 2011. Analysis of the ultralow friction behavior of a mesogenic fluid in a reciprocating contact. Wear 271, 1701–1706.
- [73] Iglesias, P., Bermúdez, M.D., Carrión, F.J., Martínez-Nicolás, G., 2004. Friction and wear of aluminium-steel contacts lubricated with ordered fluids-neutral and ionic liquid crystals as oil additives. Wear 256, 386–392.
- [74] Jiménez, A.E., Bermúdez, M.D., Carrión, F.J., Martínez-Nicolás, G., 2006. Room temperature ionic liquids as lubricant additives in steel-aluminium contacts: Influence of sliding velocity, normal load and temperature. Wear 261, 347–359.
- [75] Deshmukh, P., Lovell, M., Sawyer, W.G., Mobley, A., 2006. On the friction and wear performance of boric acid lubricant combinations in extended duration operations. Wear 260, 1295–1304.
- [76] Lovell, 2012. Tribological Performance of Environmentally Friendly Ionic Liquid Lubricants. Proceedings of the ASME, International Joint Tribology Conference
- [77] Mezger, T., 2002. The rheology handbook: for users of rotational and oscillatory rheometers. Vincentz, Hannover.

- [78] Steffe, J.F., 1992. Rheological methods in food process engineering. Freeman Press, East Lansing, Mich. USA.
- [79] Barnes, H.A., 2000. A handbook of elementary rheology. University of Wales, Institute of Non-Newtonian Fluid Mechanics, Aberystwyth.
- [80] Morrison, F.A., 2001. Understanding rheology, Topics in chemical engineering. Oxford University Press, New York.
- [81] Malvern Kinexus pro rotational rheometer [WWW Document], n.d. . URL http://www.malvern.com/labeng/products/kinexus/kinexus_rotational_rheometer.htm
- [82] Jabbarzadeh, A., Atkinson, J.D., Tanner, R.I., 1998. Nanorheology of molecularly thin films of n-hexadecane in Couette shear flow by molecular dynamics simulation. Journal of Non-Newtonian Fluid Mechanics 77, 53–78.
- [83] Anton Paar. Rheometer Brochure. 2011
- [84] Zhang, C., 2005. Research on thin film lubrication: state of the art. Tribology International 38, 443–448.
- [85] Brown, M.E., Gallagher, P.K., 2008. Handbook of thermal analysis and calorimetry. Volume 5, Recent advances, techniques and applications. Elsevier Science, Amsterdam.
- [86] Hemminger, W., Höhne, G., 1984. Calorimetry: fundamentals and practice. Verlag Chemie, Weinheim; Deerfield Beach, Fla.
- [87] Calorimetry Sciences Corporation (CSC). User Guide. Model 4100, differential scanning calorimeter.

- [88] Nishimoto, Y., Ichimura, Y., Kinoshita, R., Teramoto, Y., Yoshida, H., 1991. Heat capacity measurement by heat-flux-type DSC on cooling and heating cycles at low scan rates. Thermochimica Acta 179, 117–124.
- [89] Bhushan, B., 2002. Introduction to tribology. John Wiley & Sons, New York.
- [90] Standard test method for wear preventive characteristics of lubricating fluid (Four-Ball Method), Designation: D4172 - 94 (Reapproved 2010), ASTM International.
- [91] A screening test for anti-wear additives in a modified four-ball test. Tribotest 4, 145–158.
- [92] Standard test method for determination of the coefficient of friction of lubricants Using the Four-Ball Wear Test Machine, Designation: D 5183 – 05, ASTM International.
- [93] Dorinson, A., 1981. The nature of the wear process in the four-ball lubricant test. Wear 68, 109–127.
- [94] Archard, J.F., 1957. Elastic Deformation and the Laws of Friction. Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences 243, 190-205.
- [95] Wright, M.S., Jain, V.K., Saba, C.S., 1989. Wear rate calculation in the four-ball wear test. Wear 134, 321–334.
- [96] Lugscheider, E., Bobzin, K., 2003. Wettability of PVD compound materials by lubricants. Surface and Coatings Technology 165, 51–57.
- [97] Kirschenmann, L., Pechhold, W., 2002. Piezoelectric Rotary Vibrator (PRV) a new oscillating rheometer for linear viscoelasticity. Rheologica Acta 41, 362–368.

- [98] The Laboratory for Research on the Structure of Matter (LRSM) | FACILI-TIES: Optical Imaging and Micromanipulation [WWW Document], n.d. . URL http://www.lrsm.upenn.edu/facilities/fac_OIM.html (accessed 2.15.13).
- [99] Weitzlab Rheology Center [WWW Document], n.d. URL http://weitzlab.seas.harvard.edu/links/facilities/rheo/hrnano/index.html (accessed 3.15.13).
- [100] Bostan, L., Trunfio-Sfarghiu, A.-M., Verestiuc, L., Popa, M.I., Munteanu, F., Rieu, J.-P., Berthier, Y., 2012. Mechanical and tribological properties of poly(hydroxyethyl methacrylate) hydrogels as articular cartilage substitutes. Tribology International 46, 215–224.

Appendix A

Surface Tension

The apparatus that have been used

Fisher Scientific (Manual Model 20 Surface Tensiometer)



Surface tension of different oils





surface tension versus LCs concentration

Appendix B

Density

The apparatus that have been used

precision scale, AND-E5



Density of tested oils

	Lubricant	Density at 23°C (kg/l) +/- 0.5%
1	Mineral hydraulic oil	0.85599
2	Bio-hydraulic oil	0.9109
3	Bio-gear oil	0.91301
4	Bio-chain saw oil	0.91195
5	Engine oil	0.87422
Appendix C

Thermal Expansion

The apparatus that have been used

It was assembled in the lab



Density of water versus temperature (calibration)





Density of tested oils versus temperature

Coefficient of Thermal Expansion

	lubricant	Thermal expansion coefficient $X \ 10^{-6}$
1	Mineral hydraulic oil	756
2	Bio-hydraulic oil	746
3	Bio-gear oil	641
4	Bio-chain saw oil	756