Properties and Performance of Environmentally Adapted Synthetic Esters

Anders Pettersson
Preface

This licentiate thesis presents work that has been carried out at the Division of Machine Elements at Luleå University of Technology. The work is funded by the Foundation for strategic research, Statoil lubricants AB, Fortum Gas and Oil OY, Volvo Car Corporation, Indexator AB and SKF.

First I would to thank my supervisor Dr. Elisabet Kassfeldt and my assisting supervisor Dr. Roland Larsson and my collaborative supervisor Professor Thomas Norrby for being a valuable source of knowledge and help under this work. I would also thank Dr. Ove Andersson for help and support on the task to measure thermal properties for the tested fluids. Finally I wish to thank all my colleagues, especially my room mate Rikard Måki for invaluable support and good ideas under the time this work was carried out.

Luleå the 5th of April

Anders Pettersson
Abstract
The lubricants of the future have to be more environmentally adapted, have a higher level of performance, and lower total life cycle cost (LCC) than commonly used lubricants today. Since we live on a planet with finite resources, we have to think about coming generations and work for a sustainable development in the field of tribology. To be able to formulate those lubricants, the properties of the base fluids have to be well known. Base fluid properties that influence the formulated lubricant performance could be divided in to three different groups. These groups are; physical, chemical and film formation properties. In this study are properties from all of these groups investigated to improve the understanding on there influence on base fluid overall performance. There are more or less environmentally adapted base fluids available for formulation of lubricants. They could be divided in to different groups, mineral, semi synthetic and synthetic fluids. Synthetic fluids could be of different type: PAO (poly alpha olefins), Synthetic ester, Poly glycols and others. The most interesting group for formulation of environmentally adapted lubricants are the synthetic esters. In this thesis the properties for a large number of environmentally adapted ester base fluids are studied in detail. The tested properties relate to the macroscopic / molecular behaviour and include: viscosity-temperature-pressure-effects, $\eta(p,T)$, thermal conductivity, $\lambda(p,T)$, and heat capacity per unit volume, $c_p(p,T)$. The film formation capability in EHD contacts is also studied. Different connections between the molecular structure and the performance for the fluids are discussed. As an example, it is found that a large number of carboxylate groups in the ester molecule are improving the thermal properties, and thereby a thicker lubricating film could be maintained in highly loaded, high slip contacts.
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1 Introduction

The lubricants of the future have to be more environmentally adapted, have a higher level of performance, and lower total life cycle cost (LCC) than commonly used lubricants today. Since we live on a planet with finite resources, we have to think about coming generations and work for a sustainable development in the field of tribology. To be able to formulate these lubricants, the properties of the base fluids have to be well known, of which they can be divided into three different groups, i.e. physical, chemical, and film formation properties. This thesis contains properties from all of these investigated groups to improve the understanding on their influence of base fluid overall performance.

Tribology comes from the Greek word “tribos”, meaning rubbing, but Peter Jost first introduced the word tribology in 1966, in the well-known Jost report [1]. The Jost report focuses on the enormous losses in GNP by poor lubrication. The science of tribology is about “wear, lubrication, and friction”. Textbooks and scientific papers, such as “History of Tribology” by Dowson [2] and “History of Tribology- The Bridge between Classical Antiquity and the 21st century” by Bartz [3], extensively cover the history of tribology. The science of tribology is growing and will become more and more important in the future because of the constantly increasing demands of improved efficiency from the industry. Tribology is a wide and interdisciplinary science; in Figure 1 the position of this contribution can be located on the Map of Tribology.

1.1 Background

For most lubricated applications, the conventional choice is a mineral oil-based lubricant. Mineral oils used as lubricants have well-known properties. When a mineral oil is selected, viscosity and VI\(^1\) are normally used to characterise the fluid. If a synthetic ester-based

\(^1\) VI = Viscosity Index. VI is a measure of how much the viscosity decreases with increasing temperature.
lubricant is chosen for an application, for technical and/or environmental reasons, many additional properties might have to be evaluated in order to obtain a good result, i.e. more so for synthetic esters than for conventional mineral oils. Thermal conductivity and polarity are examples of properties that differ more between different synthetic esters than different mineral oil.

1.2 Objectives
The main objective of this thesis is to increase the understanding of how the molecular structure influences the properties for a base fluid as well as affecting the lubricity performance for the fluid. The other objective is to increase the knowledge about properties for environmentally adapted base fluids.

To improve efficiency and performance in the Swedish industry, a tribology research programme entitled HiMeC (High Performance Mechanical Components) was started. HiMeC is supported by Swedish industry and SSF (Foundations for Strategic Research). This thesis is based on the results achieved from the HiMeC project “Influence of molecular structure on lubricant properties and performance”.

2 Base fluids
All liquid lubricants are formulated with one or more base fluids as the major component. As a weighted average of all lubricants produced, the base fluid accounts for more than 95% of all lubricant formulations. But the percentage of additives in a formulation differs greatly from 1% in some simpler compressor oils to up to 30% in metalworking fluids and gear lubricants [4]. Base fluids could be of different types: mineral, synthetic, or ester, and are classified in various ways. As an example, a base fluid for use in engine oil is classified by API [5], but a fluid for formulating a hydraulic fluid is only classified by the ISO VG system [6]. In this study, several different synthetic esters, some synthetic model hydrocarbons, and one mineral reference oil are investigated.

2.1 Mineral base fluids
Mineral base fluids are produced from crude oil. The processing varies depending on the quality on the crude oil and the expected quality on the base fluid [7]. Crude oil generally consists of millions of different chemical components some are shown in Figure 2. The composition of crude oil varies depending on its origin, e.g. crude oil from South America often has a naphthenic dominance in the structure of the components while crude oil from the Middle East has more paraffinic structures.
A mineral base fluid could be of three different types as determined by the major type of chemical bond: naphthenic, aromatic, or paraffinic. The paraffinic type is most common in lubricants because of its relatively good properties. Naphthenic base fluids are sometimes used when good low temperature properties are required and not a high VI, e.g. electrical transformer oils.

White oil is an extremely high-refined mineral oil that does not contain any unsaturated structures, with all aromatics being removed by different treatments [8]. The name indicates that they are nearly colourless. White oil, used in food grade lubricants and medicinal products, has poor biodegradation and is therefore unsuitable as a base fluid for environmentally adapted lubricants. In this study, a solvent neutral (SN) mineral base fluid of paraffinic type is included as a reference.

2.1.1 Highly modified mineral fluids
Severe hydro cracking and or wax isomerization produces highly modified mineral fluids, often known as VHVI fluids [4]. In these processes, the uniformity in molecular distribution can be increased and the properties be improved compared to simpler less refined mineral products. For fluids of this type, the VI is over 120, they have low volatility, and the colour of the base fluid is light. An example of an application where VHVI base fluids are used is in semi-synthetic automotive crank case oil. The VHVI oil belongs to the Group III Base oils in the API system; however, no VHVI fluid is included in the study.

2.2 Synthetic base fluids
According to Zisman [9], synthetic base fluids were first used on an industrial scale in 1931 after Sullivan produced his research result on synthetic polymerized olefins. Many different synthetic base fluids have been invented, but the most commonly used in lubricant formulation is polyalphaolefin (PAO) and synthetic esters (SE) of different types. Cost limits the use of synthetic base fluids, where the cost of a synthetic base fluid relative to a mineral one is high; i.e. the relative cost varies from 2-3 times up to over 500. Other synthetic fluids used in lubricant applications are Poly Alkylene Glycols, (PAG), phosphate esters, and Poly Iso Butylene (PIB), but they are not included in this study.
2.2.1 Polyalphaolefin (PAO)

There are many different types of PAO, from PAO 2 to PAO 100, with the number corresponding to the viscosity in cSt at 100 °C, but for PAO 2 to PAO 10 the number also corresponds to the number of monomers. PAO is made by polymerization of 1-decene to larger molecules; see Figure 3. The term PAO was first used by the Gulf oil company and has been an internationally accepted generic appellation for hydrocarbons manufactured by catalytic oligomerization linear α-olefins [4]. Because of the increased market demand for PAO base fluids, some base fluid manufacturers have started to produce base fluids made from olefins other than 1-decene, such as mixed fractions of C₈-C₁₂ α-olefins.

![1-decene and PAO 6](image)

Characteristics for PAO are:
- High VI (over 130)
- Low volatility
- Uniform distribution of molecular weight
- Low polarity (High NPI)
- Extremely good low temperature properties
- High thermal stability

PAO has an almost ideal carbon number (and thus, molecular weight) distribution, with respect to high-temperature and low-temperature properties. Figure 4 shows the schematic molecular distribution for a mineral oil, a VHVI fluid, and a PAO 2 fluid. Low Cₓ indicates more volatile species, which worsens high-temperature properties. High Cₓ indicates heavy species which contribute to poor low-temperature properties.
When PAO was invented it was only used in a high tech application like aerospace, but in the late 1970s consumer products became available. Nowadays, PAO is used as base fluids in many high performance lubricants, synthetic motor oils, low temperature hydraulic fluids, etc. A problem with PAO is the low polarity that could lead to seal shrinkage and loss of elasticity. To overcome this problem, a synthetic ester with higher polarity could be added to the lubricant and increase the seal compatibility. No PAO base fluid is included in this investigation.

2.2.2 Vegetable oils
Prior the mid-nineteenth century almost all lubricants were derived from natural sources such as animal lard, whale oil, and vegetable oils. Today, vegetable oils remain a very important economic activity. Chemically speaking almost all vegetable oils are esters of tri-glyceride type; another important kind is wax esters. About 100 million tons of vegetable oils are produced yearly, 90% of these for use in food and 9% to produce soap. The remaining quantities are used in technical applications such as lubricants, paints, and varnish.

2.2.3 Synthetic Ester
The first synthetic esters, SE, were developed in Germany during World War II, when the available hydrocarbon fluids could not satisfy the demands for aircraft engine oils. After World War II, the development of high performing ester based fluids was closely linked to the development of aviation gas turbines. A synthetic ester in its simplest form consists of two things, an alcohol and one fatty acid. In lubricant applications esters are normally made with two or more carboxylate groups. TMP oleate which is a commonly used environmentally adapted base fluid, is made from the alcohol trimethylol propane and three fatty acid molecules, ideally oleic acid. Figure 5 shows the ester reaction for TMP oleate.
Figure 5. The ester reaction for TMP oleate

Synthetic esters are a broad range of base fluids and properties that vary greatly depending on the chemical structure. Because of the large number of different alcohols and fatty acids available for ester formulation, ester properties could be tailor-made to fit a certain application. To be able to produce tailor-made ester based fluids, understanding the connection between the molecular structure and the various properties is necessary. Synthetic esters often have a high VI; therefore, the VI improvers are often excluded. Excluding the VI improver is especially beneficial in highly loaded high shear contacts where the VI improver is often sheared down. When switching to environmentally adapted fluids, synthetic esters are the most interesting alternative to traditional base fluids because of their high quality, “tuneable” properties, no toxicity, and excellent biodegradation. Synthetic esters could provide both the performance level needed and composition to satisfy the environmental aspects demanded of future lubricants.

2.2.4 Complex Esters

One way to get a high viscosity ester base fluid is by polymerization to complex esters. The class of esters known as complex esters are really low molecular weight polyesters. Regular polyesters (e.g. in clothing) have a molecular weight of about 10000 to 1000000 (g/mol), and thousands of repeating units. In the case of complex esters a small amount of di-acid is present in the esterification process, implying that a small number of bridged species are formed, see Figure 6. This increases the viscosity from 50 cSt to between 5000 and 50000 cSt, depending on the amount of di-acid and other process parameters. However, to keep the readily biodegradable properties the viscosity should not be increased to over approximately 1100 cSt.
In this study, a number of synthetic esters are studied in detail. Di-esters, polyol-esters, and complex esters are included, along with both saturated and unsaturated ester fluids.

3 Structure and function relationship

For a lubricant, the molecular structure is closely related to the properties; Figure 7 shows the molecular structure for four different ester based fluids. Some of the properties directly related to the molecular structure are shown in Table 1. If comparing structure A to B, the molecular formula is the same, but the degree of branching is different. Branched structures like in B are beneficial for low temperature properties by preventing crystallization, but unfortunately they also decrease the viscosity index. A comparison of structure C to structure D indicates a relationship between the fatty acid chain length and the viscosity. An increased chain length increases the viscosity and the viscosity index, but the pour point is unaffected because of the presence of double bonds in the carbon chain that prevent crystallization.

Table 1. Selected properties for the fluids from Figure 7

<table>
<thead>
<tr>
<th>#</th>
<th>VI</th>
<th>Pour point</th>
<th>Viscosity, cSt @ 40 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>218</td>
<td>+4</td>
<td>8.29</td>
</tr>
<tr>
<td>B</td>
<td>123</td>
<td>-78</td>
<td>7.7</td>
</tr>
<tr>
<td>C</td>
<td>140</td>
<td>-53</td>
<td>20.0</td>
</tr>
<tr>
<td>D</td>
<td>181</td>
<td>-54</td>
<td>43.8</td>
</tr>
</tbody>
</table>

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Another example of how the fatty acid chain affects the properties could be found by comparing the NPG based (Neopentyl glycol) esters in Figure 8. These two esters have the same base viscosity at 40 °C, but the pour point and viscosity index differ. The pour point is lowered from -24 °C for the straight-chained NPG C16-C18 to -42 °C for the branched NPG ISO C18. Branching also affects the VI, which is lowered from 158 to 148.
4 Properties

Base fluid properties that influence the formulated lubricant performance can be divided into three groups, viz. physical, chemical, and film formation properties. These groups could also be divided into some subgroups to simplify the categorization of properties.

4.1 Rheological properties

The rheological properties for a base fluid are mainly viscosity and how it is affected by pressure, temperature, and shear rate. Two kinds of viscosity could be defined, kinematic and dynamic viscosity. The dynamic viscosity can be converted to kinematic viscosity by dividing it with the density.

\[ \kappa = \frac{\eta}{\rho} \]

The standard parameters that are normally measured by the lubrication industry are kinematic viscosity at 40 °C and 100 °C and density. The Viscosity Index (VI) can be calculated from the two viscosity values, as according to the ASTM standard D-2270 [10]. The manufacturer has provided the base fluid viscosity and density for the fluids tested in this study.

4.2 Chemical properties

Commonly used chemical properties for base fluids are molecular weight, molecular formula, and Non-Polarity Index (NPI), [11]. The non-polarity index is calculated as shown in the equation.

\[ \text{NPI} = \frac{\text{Total number of C atoms} \times \text{Molecular weight}}{\text{Number of carboxylic groups} \times 100} \]

The Non-Polarity Index rates the polarity for a molecule, where a low number corresponds to a highly polar molecule and a high number indicates that the molecule is non-polar. Non-Polarity Indexes for lubricants range from about 50 for short synthetic esters up to over 300 for PAO². Detergents and friction modifiers are highly polar molecules that are often used as additives in lubricants. Using a highly polar base fluid with these kinds of additives leads to competition between the base fluid and the additives for access to the surface. Other problems that could occur by using the wrong polarity in the base fluid are problems with seal swell or shrinkage and reduction of seal elasticity, [11].

4.3 Thermal properties

Useful thermal properties from a tribologists point of view are thermal conductivity and heat capacity. High thermal conductivity and high thermal capacity are good for film formation, especially under high slip and high load conditions. High heat capacity allows the fluid to increase its vibrational and rotational quantum state instead of increasing the temperature. High thermal conductivity increases the amount of energy that is transferred from the Elasto-Hydro-Dynamic (EHD) contact out to the surrounding material and fluid, thereby lowering the temperature in the contact zone and increasing viscosity. Synthetic esters normally have high thermal conductivity and high heat capacity as compared to mineral fluids. The measurements of the thermal properties were performed at the Department of Experimental Physics, Umeå University, Sweden.

² Assigned Non-Polarity Index (NPI) over 300
4.4 Properties related to environmental fate

What makes a base fluid environmentally adapted? In this thesis different environmental properties are considered to render a base fluid as environmentally adapted.

- Toxicity
- Biodegradability
- Relative content of renewable raw material
- Bioaccumulability and Biomagnification

Other definitions and examples of test methods for environmentally related properties can be found in a number of studies, such as [12] and [13].

4.4.1 Toxicity

The base fluid has to be non-toxic to be environmentally adaptable; most commonly used base fluids are [12]. Experience has shown that the toxicological properties of fully formulated lubricants are related to those of the base fluid and additive components. The measured toxicity of mixtures is found to be close to the sum of component toxicities.

4.4.2 Biodegradability

The base fluid should be rated as readably biodegradable by the OECD 301A/F test [14]. The OECD 301 test is a measure of biodegradation in an environment similar to that which is common in wastewater plants biological degradation process. Biodegradation varies greatly between different base fluids [15]. Synthetic esters generally have good biodegradability, though it should be noted that the biodegradability for high viscosity synthetic esters is moderate. The values for biodegradability for the tested fluids were provided from the base fluid manufactures.

4.4.3 Relative content of renewable raw material

The base stock that produces the base fluid should be renewable (made from vegetable or animal products) to some degree, preferable as high as possible (over 75% - even though a low percentage of renewable base stock is better than nothing). The amount of renewable raw material varies according to the composition of each synthetic ester. Commonly, the polyol part of the ester molecule is of petrochemical origin and thus non-renewable, but the fatty acid is of natural origin, i.e. renewable. To calculate the relative contribution of polyol and fatty acid to overall renewability (% renewable), the oxygen-to-carbonyl ester bond is “cut”, and one oxygen atom per ester group is assigned to the polyol. The fatty acid fragment begins with the carbonyl fragment (carbon-oxygen double bond).

Sometimes re-refined base oil is labelled as a renewable base stock, or rather, re-cycled, since the oils used for re-refining are originally made from petroleum. Re-refined base fluids are made by re-refining waste oil in specially equipped refineries. As an example, re-refined base fluids are used as a small part of the overall base fluid content in some hydraulic fluids. [4]

4.4.4 Bioaccumulability and Biomagnification

Bioaccumulation and biomagnification may cause severe damage to the inhabitants of an ecosystem during prolonged exposure. For biomagnification to occur, the pollutant must be [16]:

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10
- long-lived (display persistence, resistance to biodegradation)
- mobile
- soluble in fatty tissue
- biologically active

Bioaccumulation is when a substance accumulates in an organism. Biomagnification is when the accumulated substance concentrates higher up in the food chain, while the biomagnification can be high for certain substances (DDT, PCB, etc.) in some ecosystems. None of the commonly used base fluids are bioaccumulative.

5 Experiments
To obtain reliable properties for the tested base fluids a large number of experiments have to be performed. This chapter is sub-divided according to the investigated properties.

5.1 High-pressure viscosity
To determine the pressure-viscosity relationship at low shear stress, a high pressure Couette rheometer was used [17]. This apparatus consists of a rotational cylindrical viscometer, with a radial clearance of 0.1 mm, placed inside a pressure vessel. The pressure can be raised to 500 MPa, but in this study the maximum pressure was set to 400 MPa. A heater element controlled by an electronic regulator, is warped around the vessel and allows the test temperature to be raised to 80 °C. The shear rate range of the rheometer is from 0.5 to 20000 s⁻¹, but is normally limited by the maximum shear stress. A shear stress of 100 Pa was chosen, with the shear ratio being adjusted to achieve the desired shear stress. The tests were carried out isothermally at three different temperatures, 40, 60, and 80 °C. At each temperature the viscosity was measured at several different uniformly distributed pressure levels from about 1 MPa to 400 MPa, see Figure 9 for an example.

Figure 9. Example of raw data obtained from the High Pressure Viscosity (HPV) measurements
5.2 Thermal conductivity and specific heat capacity

The transient hot wire method [18] was used to simultaneously measure heat capacity per unit volume, \( \rho C_p(p,T) \), and thermal conductivity, \( \lambda(p,T) \). The tests were performed at the Division of Experimental Physics, Umeå University. The technique requires that the tested fluid be placed in a PTFE test cell where a nickel \( (\text{Ni}) \) wire, approximately 40 mm long with a diameter of 0.1 mm, is located. A 1.4 s constant power pulse is applied to the wire, and by measuring the wire’s electrical resistance vs. time, its temperature rise can be determined. An analytical solution for the temperature rise was fitted to the data points, thereby yielding \( \lambda \) and \( \rho C_p \). The accuracy is estimated to ± 2% for \( \lambda \) and ± 5% for \( \rho C_p \).

The test cell is inserted in a pressure vessel where the test pressure can then be raised up to 1 GPa. An electronic regulator was used to control the rate of pressure increase. For up to 1 GPa, a low rate of pressure increase was set, 3.3 MPa/minute, to avoid an uncontrolled temperature rise during pressurization. The operating temperature of the cell could be raised to 80 °C by heating the pressure vessel. The temperature is measured using a type K thermocouple and is controlled by an electronic regulator. Data were sampled every 150 s. Figure 10 shows the \( \lambda \)-value for some of the tested fluids up to 1 GPa.

![Figure 10. Raw data for \( \lambda \) for some of the tested fluids](image)

5.3 EHD friction coefficient

One way to determine if a lubricant has the potential for high efficiency in highly loaded contacts such as between gear flanks is to measure the EHD friction coefficient. A low EHD friction coefficient value corresponds to low frictional losses. In this study, the EHD friction coefficient for the tested fluids is measured with a “Ball and bar apparatus”. Ährström [19] developed this method for transient friction measurements, during high
pressures and as a function of time. A steel ball impacts the lubricated end plane of a slender beam and the vibration response is recorded. The data is analyzed through fast Fourier transform and second order dynamic beam theory. Time functions of both transverse and normal forces can be accurately calculated, and the friction coefficient can be obtained by calculating their relation. The tests were performed at a maximum contact pressure of 2 GPa and a temperature of 20 °C.

5.4 EHD film forming capability

A Ball & Disc apparatus was used [20] to determine the fluids’ film forming capability. In this rig, a highly polished steel ball is loaded against a transparent sapphire disc while the contact is continuously fed with lubricant. The speed of the ball-and-disc can be set independently, as to create any condition of slide-to-roll ratio. Illuminating the ball and disc contact and simultaneously monitoring it through a microscope using a CCD-camera can acquire images of the contact. Since the disc is coated with a thin layer of chromium, the incident light generates optical interference that is captured and processed digitally for the film thickness. The multi-channel method was used for this purpose [21].

All experiments were conducted at 40 °C ±0.5 °C. The speed was varied from the point that gives a central film thickness of approximately 100 nm, (0.3-0.5 m/s), up to 2.4 m/s. The lower limit is due to the minimum film thickness that can be measured using this specific setup. Thinner films may be measured with other setups. A constant load was chosen to give a maximum Hertzian pressure of 1.13 GPa. Each fluid was subjected to three different tests with a varying slide to roll ratio, A_c, of 0, 0.6, and 1.2.

Figure 11. Raw data for central film thickness at A_c = 0 and A_c = 1.2 for the tested fluids.
6 Results and discussion

6.1 Paper A

Paper A of this thesis, “Properties of base fluids for environmentally adapted lubricants” [22], contains basic measurements from the first study of environmentally adapted base fluids. Five different fluids, three synthetic esters, and two synthetic model hydrocarbons are tested. All the tested fluids have a well-defined molecular structure. The fluids are environmentally adapted to different degrees. The tested properties relate to the macroscopic / molecular behaviour and included: viscosity-temperature-pressure-effects, $\eta(p,T)$, thermal conductivity, $\lambda(p,T)$, and heat capacity per unit volume, $\rho c_p(p,T)$. This paper provided interesting information about how the properties for different base fluids vary, to be helpful in the next stage.

6.2 Paper B

Paper B, “Tribological characterization of environmentally adapted ester based fluids” [23], is an investigation of base fluids that were selected based on a strategy developed from Paper A. Six ester-based fluids and one mineral reference fluid were further investigated. All the selected fluids are suitable for formulation of hydraulic fluids. The tested properties were: viscosity-temperature-pressure-effects, $\eta(p,T)$, thermal conductivity, $\lambda(p,T)$, and heat capacity per unit volume, $\rho c_p(p,T)$, but the properties are studied in more detail in this paper. The thermal conductivity and specific heat capacity are high for the esters compared to mineral fluids. There is a strong correlation between the number of carboxylate groups and the thermal conductivity, see Figure 12.

![Figure 12. Correlation between number of carboxylate groups and lambda for the tested fluids](image-url)
6.3 Paper C

Paper C investigates the film formation properties for the fluids from Paper B, [24]. Film formation is measured in a Ball and Disc apparatus with the use of optical interferometry. The tests were conducted with a contact pressure of 1.13 GPa and under both pure rolling conditions and two different slide-to-roll ratios (A_r= 0.6 and 1.2). The best ester based fluids are sufficient in maintaining the film thickness under sliding conditions. The mineral type fluid used in the investigation is less sensitive to increased Hertzian pressure on film thickness, possibly due to solidification. Less pressure dependent esters that do not easily solidify reduce the film thickness accordingly.

6.4 Other results

Other studies have shown that the EHD transient friction coefficient is closely related to the thermal properties for a fluid, [25]. This could lead to further conclusions, possibly direct correlations between EHD transient friction coefficient and the number of carboxylate groups and some molecular weight parameters.

7 Conclusions

Environmentally adapted synthetic ester fluids generally have properties that are suitable for the formulation of lubricants, especially for applications operating over a wide temperature range. The best synthetic ester fluids in this investigation generally maintain the film thickness better under severe sliding conditions than mineral based fluids at a constant temperature; however, should the temperature be increased, the difference will be even greater.

The results of this investigation show that environmentally adapted fluids have good and stable properties and are suitable for formulation of the lubricants of tomorrow.

7.1 Future work

To be able to produce tailor-made environmentally adapted ester based fluids, more information about the relationship between the properties and the molecular structure will be needed, thereby requiring further investigations and the inclusion of other properties.

8 References


[5] API Standard: 1509, American Petroleum Institute, 1220 L Street, NW Washington, DC 20005-4070, USA


[14] OECD Bookshop, 2 rue André Pascal, Paris, Cedex 16, 75775, France


Thesis

This thesis on the subject environmentally adapted base fluids is based on the following papers:

Paper A, (revised version)

Paper B

Paper C
Pettersson, A., Lord, J., Kassfeldt, E., “Film formation capability of environmentally adapted base fluids”, submitted for publication.
Paper A
PROPERTIES OF BASE FLUIDS FOR ENVIRONMENTALLY ADAPTED LUBRICANTS

A. Pettersson\(^1\), R. Larsson\(^2\), T. Norrby\(^3\) and O. Andersson\(^4\)
\(^1\)Luleå University of Technology, Division of Machine Elements, SE-971 87 Luleå, Sweden, e-mail: ap@mt.luth.se.
\(^2\)Statoil Lubricants R&D, SE-149 22 Nynäshamn, Sweden.
\(^3\)Dep. of Experimental Physics, Umeå University, SE-901 87 Umeå, Sweden.

SUMMARY

Five different fluids, two hydrocarbons and three ester based fluids, suitable for use as base oils for environmentally adapted lubricants have been investigated. The fluids are environmentally adapted to different degree, and have a well-defined molecular structure. The tested properties relate to the macroscopic/molecular behaviour and included: viscosity-temperature-pressure-effects, \(\eta(p, T)\), thermal conductivity, \(\lambda(p,T)\) and heat capacity per unit volume, \(\rho c_p(p,T)\).

Keywords: lubrication, environmentally adapted lubricants, EAL, viscosity, pressure-viscosity, thermal conductivity

1 INTRODUCTION

Future lubricants are expected to be environmentally adapted whilst maintaining good performance characteristics. The properties of different base fluids vary widely and it is important to understand the effects of these on the performance of a lubricant in the full film and mixed lubrication regimes. To be able to select an appropriate lubricant quickly and efficiently, the properties of the base fluid have to be considered. Base oil properties can be divided into a number of different groups: Lubrication, physical, molecular, and environmental. In this investigation lubrication properties have not been included. Physical properties are those related to transport and state. To be able to perform EHL analyses, the effects of pressure on different properties must be known. It would be of great value if the coupling between physical properties and molecular properties were better understood. In the present work, measurements of some of the most important physical properties have been carried out on five synthetic and pure base fluids. This allows correlation between the physical and rheological properties against the molecular structure.

2 FLUIDS

Five different fluids have been investigated (see Table 1 and Fig.1). All the fluids have well-defined molecular structure, are environmentally acceptable to different degrees and are potential base fluids, or model compounds for base fluids.

<table>
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<th>#</th>
<th>Fluid</th>
<th>(\eta_{25} \text{[mPa} \cdot \text{s]})</th>
<th>M-formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Bis (2-ethyl hexyl) sebacate</td>
<td>10.08</td>
<td>(\text{C}<em>{26}\text{H}</em>{50}\text{O}_{4})</td>
</tr>
<tr>
<td>B</td>
<td>Triocetyl methane</td>
<td>6.6</td>
<td>(\text{C}<em>{30}\text{H}</em>{52})</td>
</tr>
<tr>
<td>C</td>
<td>2,6,10,15,19,23-Hexamethyltetraicosane</td>
<td>15.6</td>
<td>(\text{C}<em>{30}\text{H}</em>{62})</td>
</tr>
<tr>
<td>D</td>
<td>TMP Oleate</td>
<td>50</td>
<td>(\text{C}<em>{60}\text{H}</em>{110}\text{O}_{6})</td>
</tr>
<tr>
<td>E</td>
<td>TMP C8/C10</td>
<td>19</td>
<td>(\text{C}<em>{12}\text{H}</em>{26}\text{O}_{6})</td>
</tr>
</tbody>
</table>

Table 1 The investigated base fluids

Non of the base fluids contain additives. Bis (2-ethyl hexyl) sebacate was chosen as a reference or calibration fluid for the viscosity measurements, since its viscosity-pressure relationship is well known [1], [2]. The sebacate is a synthetic diester and is available in a highly pure form. Fluids B (synthetic) and C (Squalene, a natural product) are pure hydrocarbons with different molecular weights and structures. Fluids D and E are synthetic tri-esters, both based on the alcohol trimethylol propane (TMP), esterified with fatty acids of natural origin with different chain lengths and saturation/unsaturation patterns.

3 EXPERIMENTAL METHODS

The fluid characteristics that were determined included, viscosity-temperature-pressure-effects, \(\mu(p, T)\), thermal conductivity \(\lambda(p,T)\), heat capacity per unit
volume, \( \rho_{cp}(p, T) \), density, different molecular parameters and environmental properties.

### 3.1 High pressure viscosity measurements

To determine the pressure-viscosity relationship at low shear stress, a high pressure Couette rheometer was used [3]. This apparatus consists of a rotational cylindrical viscometer, with a radial clearance of 0.1 mm, which is placed inside a pressure vessel. The pressure can be raised to 500 MPa but 400 MPa is a more normal working pressure. A heater element, which is controlled by an electronic regulator, is warped around the vessel and allows the test temperature to be raised to 80°C. The shear ratio range of the rheometer is from 0.5 to 2000 s\(^{-1} \), but is limited by the maximum shear stress. The apparatus was calibrated using fluid A, which was used as a reference for the other measurements [1-2].

The temperature-pressure- and viscosity data \( \eta(p, T) \) were parameterized against the Roelands pressure-viscosity equation [4]:

\[
\eta(p, T) = \eta_0 (T) e^{\left( \ln(\eta_0 (T)) + 9.67 \right) - (1.51 \times 10^{-9} p) Z(T)}
\] (1)

This relationship is a good empirical model for the pressure range covered in this investigation. It should not, however, be used to extrapolate data to higher pressures [1].

The viscosity at ambient pressure \( \eta_0(T) \) can be obtained from:

\[
\eta_0 = 10^{(a + 2)}
\] (2)

The parameter \( Z(T) \) was obtained from:

\[
Z(T) = D_Z - C_Z \log \left( \frac{T}{135} \right)
\] (3)

Roelands equation describes a lubricant’s pressure-temperature- and viscosity relationship with four coefficients: \( S_0 \), \( G_0 \), \( D_Z \), and \( C_Z \). A shear stress of 100 Pa was chosen, with the shear ratio being adjusted to achieve the desired shear stress. The tests were carried out isothermally at three different temperatures, 40, 60 and 80°C. At each temperature the viscosity was measured at several different pressure levels uniformly distributed from about 1 MPa to 400 MPa, see Fig. 2.

If the coefficients in Roelands equation for a given lubricant are known, it is possible to calculate the viscosity for any temperature and pressure within the limits of the measurement range. It is thus possible to calculate both the pressure-viscosity coefficient, \( \alpha \) and the temperature-viscosity coefficient, \( \beta \) for any pressure and temperature. The \( \alpha \) value is defined from the Barus expression:

\[
\eta = \eta_0 e^{\alpha p}
\] (4)

The value of \( \alpha \) can be obtained from equation (1) as:

\[
\alpha(p, T) = \frac{1}{p} \left( \ln(\eta_0(T)) + 9.67 \right) - (1 + 5.1 \times 10^{-9} p) Z(T)
\] (5)

The value of \( \beta \) is defined as:

\[
\eta(T) = \eta_0 e^{-\beta(T-T_0)}
\] (6)

Where \( \eta_0 \) is the dynamic viscosity at 40°C and \( T_0 \) is 40°C.

### 3.2 Thermal conductivity and heat capacity

The transient hot wire method [5] was used to measure heat capacity per unit volume, \( \rho_{cp}(p, T) \), and thermal conductivity, \( \lambda(p, T) \), simultaneously. The technique requires that the tested fluid is placed in a PTFE test cell in which a Nickel (Ni) wire, approximately 40 mm long with a diameter of 0.1mm is located. A 1.4 s constant power pulse is applied to the wire and by measuring the wire’s resistance against time, its temperature rise can be determined. (These data can then be fitted to a theoretical expression from which heat capacity per unit volume and thermal conductivity can be determined.)

An analytical solution for the temperature rise was fitted to the data points, thereby yielding \( \lambda \) and \( \rho_{cp} \). The accuracy is estimated to ca. ± 2% for \( \lambda \) and ca. ± 5% for \( \rho_{cp} \).

By placing the test cell in a pressure vessel the pressure could be raised up to 1 GPa. An electronic regulator was used to control the rate of pressure increase with the rate up to 1 GPa being set to 3.3 MPa/minute; necessary to avoid uncontrolled temperature rise during pressurization. The operating temperature of the cell could be raised to 80°C by heating the pressure vessel. The temperature is measured using a type K thermocouple and is controlled by an electronic regulator. Data were collected every 150 s and stored in a file.

### 3.3 Density measurements

The density-temperature relationship for the tested oils was measured at atmospheric pressure with a standard pycnometer. The pycnometer was first weighed empty then filled with oil and placed in an electric oven for several hours. When the oil had reached the test temperature the pycnometer was weighed again and the density calculated. The density was determined at 40, 60, 80 and 100°C. The result was parameterized in to a density temperature relationship:
\[ \rho(T) = \rho_{15} + \frac{\rho}{d\rho / dT} (T - 15) \]  

(7)

3.4 Viscosity-temperature at ambient pressure
To be able to calculate the Viscosity Index, and to obtain additional information about the viscosity-temperature relationship, \( \eta(T) \) a test in a Bohlin CS Rotational viscometer was carried out. Tests were performed at constant temperature and with a shear stress range from 10 to 1000 s\(^{-1}\). The lubricants were tested at 40, 60 and 80°C.

3.5 Molecular parameters
The following molecular parameters were determined; non-polarity index, molecular mass and the number of carboxylate groups. The non-polarity index (NPI) is defined as [6]:

\[ \text{NPI} = \frac{\text{Total number of } C \text{ atoms} \times \text{Molecular weight}}{\text{Number of carboxylic groups} \times 100} \]  

(8)

The two pure hydrocarbons have no carboxylate groups and the synthetic esters studied have either two or three, see Table 2.

<table>
<thead>
<tr>
<th>#</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPI</td>
<td>55</td>
<td>~300</td>
<td>~300</td>
<td>186</td>
<td>72</td>
</tr>
<tr>
<td>Mw</td>
<td>426.37</td>
<td>352.41</td>
<td>422.49</td>
<td>926.83</td>
<td>540.44</td>
</tr>
<tr>
<td>COOR</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 2. Molecular properties

### 4 RESULTS

4.1 High pressure viscosity
The parameters obtained from curve fitting Roelands equation are presented in Table 3.

<table>
<thead>
<tr>
<th>#</th>
<th>S(_0)</th>
<th>G(_0)</th>
<th>C(_r)</th>
<th>D(_r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.8563</td>
<td>2.8898</td>
<td>-0.0086</td>
<td>0.5368</td>
</tr>
<tr>
<td>B</td>
<td>0.7455</td>
<td>2.543</td>
<td>0.2111</td>
<td>0.5834</td>
</tr>
<tr>
<td>C</td>
<td>1.0133</td>
<td>3.3433</td>
<td>-0.0521</td>
<td>0.6187</td>
</tr>
<tr>
<td>D</td>
<td>0.7338</td>
<td>3.5151</td>
<td>0.1889</td>
<td>0.4865</td>
</tr>
<tr>
<td>E</td>
<td>0.8495</td>
<td>3.1578</td>
<td>0.0713</td>
<td>0.5246</td>
</tr>
</tbody>
</table>

Table 3. Roelands coefficients for the lubricants

The \( \alpha \) value is obtained from Equation 5, see Table 4.

<table>
<thead>
<tr>
<th>#</th>
<th>( \alpha@20^\circ C )</th>
<th>( \alpha@80^\circ C )</th>
<th>( \alpha@20^\circ C )</th>
<th>( \alpha@80^\circ C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.62 \times 10^{-3}</td>
<td>1.20 \times 10^{-8}</td>
<td>1.22 \times 10^{-8}</td>
<td>0.91 \times 10^{-8}</td>
</tr>
<tr>
<td>B</td>
<td>1.61 \times 10^{-3}</td>
<td>1.24 \times 10^{-8}</td>
<td>1.32 \times 10^{-8}</td>
<td>1.04 \times 10^{-8}</td>
</tr>
<tr>
<td>C</td>
<td>2.10 \times 10^{-3}</td>
<td>1.64 \times 10^{-8}</td>
<td>1.49 \times 10^{-8}</td>
<td>1.16 \times 10^{-8}</td>
</tr>
<tr>
<td>D</td>
<td>1.86 \times 10^{-3}</td>
<td>1.35 \times 10^{-8}</td>
<td>1.54 \times 10^{-8}</td>
<td>1.14 \times 10^{-8}</td>
</tr>
<tr>
<td>E</td>
<td>1.74 \times 10^{-3}</td>
<td>1.29 \times 10^{-8}</td>
<td>1.35 \times 10^{-8}</td>
<td>1.00 \times 10^{-8}</td>
</tr>
</tbody>
</table>

Table 4. \( \alpha \) values

The \( \beta \) value was calculated from Equation 6, see Table 5 for some examples.

<table>
<thead>
<tr>
<th>#</th>
<th>( \beta ) ( p=0 \text{ MPa} )</th>
<th>( \beta ) ( p=400 \text{ MPa} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.0225</td>
<td>0.0391</td>
</tr>
<tr>
<td>B</td>
<td>0.0235</td>
<td>0.0293</td>
</tr>
<tr>
<td>C</td>
<td>0.0275</td>
<td>0.0561</td>
</tr>
<tr>
<td>D</td>
<td>0.0287</td>
<td>0.0364</td>
</tr>
<tr>
<td>E</td>
<td>0.0270</td>
<td>0.0406</td>
</tr>
</tbody>
</table>

Table 5. \( \beta \) values

4.2 Thermodynamical properties
The thermal conductivity and heat capacity per unit volume at ambient pressure are presented in Table 6.

<table>
<thead>
<tr>
<th>#</th>
<th>( \lambda_{\text{at}} ) [W/m °C]</th>
<th>( \rho C_{\text{at}} ) [J/(m°C)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.143</td>
<td>1.81 \times 10^6</td>
</tr>
<tr>
<td>B</td>
<td>0.153</td>
<td>1.76 \times 10^6</td>
</tr>
<tr>
<td>C</td>
<td>0.123</td>
<td>1.68 \times 10^6</td>
</tr>
<tr>
<td>D</td>
<td>0.164</td>
<td>1.84 \times 10^6</td>
</tr>
<tr>
<td>E</td>
<td>0.148</td>
<td>1.86 \times 10^6</td>
</tr>
</tbody>
</table>

Table 6. Thermodynamic data

The plotted raw data for the thermal conductivity and heat capacity per unit volume up to 1 GPa are shown in Figs 3 and 4. As can be seen in Fig. 4, fluid B is the only fluid with a transition in the investigated pressure range. This transition is due to crystallization, and is seen as a jump in the thermal conductivity curve.

Figure 3. Thermal conductivity as a function of pressure at 20°C.

Figure 4. Heat capacity per unit volume as a function of pressure at 20°C.

4.3 Density measurements
The density parameters were calculated from the pycnometer measurements, see Table 7. All
investigated fluids have a linear density variation with temperature.

<table>
<thead>
<tr>
<th></th>
<th>( \rho ) 15°C [kg/m³]</th>
<th>dp/dT</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>917</td>
<td>-0.697</td>
</tr>
<tr>
<td>B</td>
<td>804</td>
<td>-0.603</td>
</tr>
<tr>
<td>C</td>
<td>811</td>
<td>-0.619</td>
</tr>
<tr>
<td>D</td>
<td>920</td>
<td>-0.631</td>
</tr>
<tr>
<td>E</td>
<td>945</td>
<td>-0.609</td>
</tr>
</tbody>
</table>

Table 7. Density data

<table>
<thead>
<tr>
<th></th>
<th>Renewable [%]</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Estimated biodegradability.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 8. Biodegradability and relative amount of renewable raw material.

4.4 Environmental properties

There are many ways to characterize a fluid from an environmental perspective. In this paper biodegradability and the amount of renewable raw material have been considered. Biodegradability measures were based on OECD 301 B/F, see Table 8. In the synthetic esters D and E, the polyol alcohol is a non-renewable raw material, whilst the fatty acids are.

Below are the gum consistency values for the synthetic esters D and E, the polyol alcohol is a non-renewable raw material, whilst the fatty acids are.

The EHL friction coefficient \( \gamma \) is shown in Table 9 [8]. Fluid C has, for example, almost twice as high \( \gamma \)-value as D, and use of D instead of C will thus reduce the EHL friction to 50%.

<table>
<thead>
<tr>
<th></th>
<th>( \gamma ) at 2GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.047</td>
</tr>
<tr>
<td>B</td>
<td>0.038</td>
</tr>
<tr>
<td>C</td>
<td>0.056</td>
</tr>
<tr>
<td>D</td>
<td>0.031</td>
</tr>
<tr>
<td>E</td>
<td>0.042</td>
</tr>
</tbody>
</table>

Table 9. EHL friction coefficients at 20°C

The influence of the different base oil properties on lubrication parameters are presented in Table 10 [7]. It shows how different properties should be optimized. “High” means that a high value is preferable, “Low” means low value is preferable and “H/L” means its influence is ambiguous. Fluid C has the highest \( \alpha \)-value and its molecular structure is representative for an iso-paraffinic hydrocarbon. A high \( \alpha \)-value is beneficial for film build-up, but results in higher friction.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( \eta_0 )</th>
<th>( \alpha )</th>
<th>( \beta )</th>
<th>( \rho_{\text{velo}} )</th>
<th>( \lambda_\text{H/L} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film thickness</td>
<td>High</td>
<td>High</td>
<td>Low</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Friction</td>
<td>Low</td>
<td>Low</td>
<td>H/L</td>
<td>?</td>
<td>H/L</td>
</tr>
<tr>
<td>Pressure peaks</td>
<td>H/L</td>
<td>Low</td>
<td>?</td>
<td>?</td>
<td>?</td>
</tr>
</tbody>
</table>

Table 10. Influence of different properties on lubrication parameters

It is to early to draw any general conclusions about the coupling between molecular parameters and the physical properties, but future investigations will give further understanding of the important mechanisms.

6 ACKNOWLEDGEMENTS

The authors wish to express thanks to The Swedish Foundation for Strategic Research for financing this project. We would also like to thank Statoil Lubricants and Mobil Oil for supplying the tested fluids.

7 REFERENCES

Paper B
Tribological characterization of environmentally adapted ester based fluids

Anders Pettersson *
Sirius Laboratory, Division of Machine Elements, Luleå University of Technology, SE-971 87 Luleå, Sweden

Abstract

Fundamental properties of six synthetic ester base fluids, suitable for the formulation of environmentally adapted lubricants, have been investigated. High pressure viscosity data for the test fluids were obtained through experimental measurements with a high pressure Couette rheometer. The temperature, pressure and viscosity data \( \eta(p, T) \) were parameterized against the Roelands pressure-viscosity equation. Thermal conductivity and specific heat capacity data were obtained using a transient hotwire method, and the EHD friction coefficient, \( \gamma \), was obtained experimentally as well. The results from these measurements are reported, and the correlation between thermal properties, molecular structure, and the fluid rheology parameters, of the test fluids are discussed.

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Keywords: Base oil; Environmentally adapted; Polyol ester; Synthetic ester; Thermodynamic properties

1. Introduction

Environmentally adapted lubricants have become more and more important in industrial applications. To meet the market demand and be able to develop new and highly efficient environmentally adapted fluids, the properties of the base fluid should be well known. The properties of different base fluids vary widely and it is important to understand the effects of these on the performance of a lubricant in the full film and mixed lubrication regimes. To be able to perform EHD calculations, the effect of pressure on different properties must be known. It would be of great value if the coupling between physical properties and molecular properties were better understood.

Base fluid properties can be divided into a number of different groups: lubrication, physical, molecular, and environmental. In this investigation, no lubrication properties are included.

In this study, properties for seven different base fluids, six esters and one mineral fluid are investigated. All fluids are suitable as base fluids for synthetic hydraulic fluids.

2. Tested fluids

The different fluids chosen for investigation in this study are listed in Table 1. All the fluids are in the ISO VG 46 range of viscosity except fluid I which is an ISO VG 68. The suppliers of the fluids provide information about density at 15 °C and kinematic viscosity at 40 and 100 °C.

Bis-(2-ethyl-hexyl) sebacate was chosen as calibration fluid for the viscosity measurements, since its viscosity-pressure relationship is well known [1,2]. The sebacate is a synthetic diester and is available in a highly pure form. Fluids G and H are synthetic triesters based on the alcohol trimethylol propane (TMP) with mostly oleic
acid tails (C18:1). The improved TMP oleate is partly complex. Fluid I, the PE oleate is a tetraester based on pentaerythiol and oleic acid tails (C18:1). Fluids J and K is diester based on neopentylglycol (NPG) and different fatty acids. Fluid L is a complex ester based on 2-ethyl-2-butyl-1,3-propanediol and sebacic and octanoic acid.

The last fluid, M is a mineral oil reference, paraffinic and solvent neutral refined. Some of the tested fluids are shown in Fig. 1, since fluids H, L and M do not have an exact molecular structure they are excluded from the figure.

The following molecular parameters were determined: non-polarity index (NPI), molecular mass and the number of carboxylate groups. The NPI is defined as [3]:

\[
\text{NPI} = \frac{\text{Total number of C atoms} \times \text{Molecular weight}}{\text{Number of carboxylic groups} \times 100}
\]

The mineral oil has no carboxylate groups and the synthetic esters studied have two, three or four, see Table 2.

The data provided from the base fluid suppliers are found in Table 3.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Carboxylate groups</th>
<th>Molecular weight</th>
<th>Non-polarity index</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>3</td>
<td>927.5</td>
<td>185.5</td>
</tr>
<tr>
<td>H</td>
<td>-3</td>
<td>~900</td>
<td>~180</td>
</tr>
<tr>
<td>I</td>
<td>4</td>
<td>1193.9</td>
<td>229.8</td>
</tr>
<tr>
<td>J</td>
<td>2</td>
<td>637.1</td>
<td>130.6</td>
</tr>
<tr>
<td>K</td>
<td>2</td>
<td>609.0</td>
<td>118.8</td>
</tr>
<tr>
<td>L</td>
<td>N/A</td>
<td>~720</td>
<td>N/A</td>
</tr>
<tr>
<td>M</td>
<td>0</td>
<td>N/A</td>
<td>~250</td>
</tr>
</tbody>
</table>

Fig. 1. Schematic figures of molecular structure of fluids G, I, J and K.
Table 3
Base fluid specifications

<table>
<thead>
<tr>
<th>#</th>
<th>$v_{10}$ (cSt)</th>
<th>$v_{100}$ (cSt)</th>
<th>VI</th>
<th>$\rho$ at 15°C (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>43.78</td>
<td>8.64</td>
<td>158</td>
<td>918</td>
</tr>
<tr>
<td>H</td>
<td>48.16</td>
<td>9.45</td>
<td>184</td>
<td>931</td>
</tr>
<tr>
<td>I</td>
<td>71.64</td>
<td>12.9</td>
<td>183</td>
<td>925</td>
</tr>
<tr>
<td>J</td>
<td>45.38</td>
<td>8.87</td>
<td>180</td>
<td>904</td>
</tr>
<tr>
<td>K</td>
<td>42.00</td>
<td>7.80</td>
<td>158</td>
<td>907</td>
</tr>
<tr>
<td>L</td>
<td>44.05</td>
<td>7.75</td>
<td>146</td>
<td>948</td>
</tr>
<tr>
<td>M</td>
<td>46.79</td>
<td>5.98</td>
<td>55</td>
<td>873</td>
</tr>
</tbody>
</table>

3. Test methods

The fluid characteristics that were determined included viscosity—temperature—pressure effects, $\eta(p,T)$, thermal conductivity $\lambda(p,T)$, heat capacity per unit volume, $\rho C_p(p,T)$, density, different molecular parameters and environmental properties.

3.1. High pressure viscosity measurements

To determine the pressure—viscosity relationship at low shear stress, a high pressure Couette rheometer was used [4]. This apparatus consists of a rotational cylindrical viscometer, with a radial clearance of 0.1 mm, which is placed inside a pressure vessel. The pressure can be raised to 500 MPa and in this study the maximum pressure was set to 400 MPa. A heater element, which is controlled by an electronic regulator, is warped around the vessel and allows the test temperature to be raised to 80°C. The shear rate range of the rheometer is from 0.5 to 20 000 s⁻¹, but is limited by the maximum shear stress. A shear stress of 100 Pa was chosen, with the shear ratio being adjusted to achieve the desired shear stress. The tests were carried out isothermally at three different temperatures, 40, 60 and 80°C. At each temperature, the viscosity was measured at several different pressure levels uniformly distributed from about 1 to 400 MPa, see Fig. 2 for an example.

The apparatus was calibrated using Bis-(2-ethylhexyl) sebacate, which was used as a reference for the other measurements [1]. The temperature, pressure, and viscosity data $\eta(p,T)$ were parameterized against the Roelands pressure—viscosity equation [5]. Roelands equation describes a lubricant’s pressure—temperature—viscosity relationship with four coefficients: $S_0$, $G_0$, $D_z$ and $C$, $\eta(p,T) = \eta_0(T)e^{S_0 \log(1 + \frac{T}{135}) + 9.671(1 + 5.1 \times 10^{-9}pZ(T))}$ (2)

This relationship is a good empirical model for the pressure range covered in this investigation. It should not, however, be used to extrapolate data to higher pressures [1].

The viscosity at ambient pressure $\eta_0(T)$ can be obtained from:

$$\eta_0 = 10^{(\eta_{10}(40°C) + 2)}; \text{ where } a = -S_0 \log\left(1 + \frac{T}{135}\right) + \log G_0$$

The parameter $Z(T)$ was obtained from:

$$Z(T) = D_z - C \log\left(1 + \frac{T}{135}\right)$$

3.2. The use of Roelands equation

If the coefficients in Roelands equation for a given lubricant are known, it is possible to calculate the viscosity for any temperature and pressure within the limits of the measurement range. It is thus possible to calculate both the pressure—viscosity coefficient, $\alpha$, and the temperature—viscosity coefficient, $\beta$, for any pressure and temperature. The $\alpha$-value is defined in the Barus expression:

$$\eta = \eta_0 e^{\alpha p}$$

The value of $\alpha$ can be obtained from Eq. (2) as

$$\alpha(p,T) = \frac{1}{p}(\ln(\eta_0(T)) + 9.67)(1 + 5.1) \times 10^{-9}pZ(T))$$

The value of $\beta$ is calculated from

$$\eta(T) = \eta_0 e^{-\beta(T-T_0)}$$

where $\eta_0$ is the dynamic viscosity at 40°C and ambient pressure, and $T_0$ is 40°C.
3.3. Thermal conductivity and specific heat capacity

The transient hotwire method [6] was used to measure heat capacity per unit volume, $\rho C_p(p, T)$, and thermal conductivity, $\lambda(p, T)$, simultaneously. The technique requires that the tested fluid is placed in a PTFE test cell in which a nickel (Ni) wire, approximately 40 mm long with a diameter of 0.1 mm, is located. A 1.4 s constant power pulse is applied to the wire, and by measuring the wire's electrical resistance vs. time its temperature rise can be determined. An analytical solution for the temperature rise was fitted to the data points, thereby yielding $\lambda$ and $\rho C_p$. The accuracy is estimated to 2% for $\lambda$ and 5% for $\rho C_p$.

The test cell is inserted in a pressure vessel and then the test pressure can be raised up to 1 GPa. An electronic regulator was used to control the rate of pressure increase. Up to 1 GPa, a low rate of 3.3 MPa/min was set, in order to avoid uncontrolled temperature rise during pressurization. The operating temperature of the cell was raised to 80 °C by heating the pressure vessel. The temperature is measured using a type K thermocouple and is controlled by an electronic regulator. Data were sampled every 150 s.

3.4. EHD friction coefficient

The EHD friction coefficient $\gamma$ for the fluids was measured with a "Ball and bar apparatus". This method for transient friction measurements, during high pressures and as a function of time, has been developed by Åhrström [7]. A steel ball impacts the lubricated end plane of a slender beam and the vibration response is recorded. The data are analyzed through fast Fourier transform and second order dynamic beam theory. Time functions of both transverse and normal forces can be calculated, with high accuracy, and the friction coefficient can be obtained by forming their relation. The tests were performed at a maximum contact pressure of 2 GPa and a temperature of 20 °C.

4. Results

The results are divided into the following groups, high pressure viscosity, thermodynamic properties, EHD friction and environmental properties.

4.1. High pressure viscosity

The parameters obtained from curve fitting Roelands equation are presented in Table 4. The $\alpha$-values were calculated with help of Eq. (6), for ambient pressure and temperature and for one higher pressure level and one raised temperature, see Table 5. The $\beta$-values were calculated from Eq. (7), for ambient pressure and for one higher pressure level, see Table 6.

4.2. Thermodynamic properties

The thermal conductivity and heat capacity per unit volume at ambient pressure and two different temperatures are presented in Table 7.

The plotted raw data for the thermal conductivity and heat capacity per unit volume up to 1 GPa and at 20 °C are shown in Figs. 3 and 4.

4.3. EHD friction coefficient

Table 6 shows the EHD friction coefficients for the tested fluids, tested at 20 °C and with a pressure of 2 GPa.

3.3. Thermal conductivity and specific heat capacity

<table>
<thead>
<tr>
<th>#</th>
<th>$\alpha$ at 20 °C</th>
<th>$\alpha$ at 40 °C</th>
<th>$\alpha$ at 80 °C</th>
<th>$\alpha$ at 20 °C</th>
<th>$\alpha$ at 40 °C</th>
<th>$\alpha$ at 80 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>H</td>
<td>0.7697</td>
<td>3.4706</td>
<td>0.0902</td>
<td>0.4717</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>0.7576</td>
<td>3.619</td>
<td>-0.0824</td>
<td>0.4272</td>
<td></td>
<td></td>
</tr>
<tr>
<td>J</td>
<td>0.9468</td>
<td>3.6202</td>
<td>0.0013</td>
<td>0.5238</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>L</td>
<td>0.7876</td>
<td>3.4276</td>
<td>0.111</td>
<td>0.5359</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>1.1912</td>
<td>3.7403</td>
<td>-0.1144</td>
<td>0.6367</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>#</th>
<th>$\beta$ at 0 MPa, 40-80</th>
<th>$\beta$ at 400 MPa, 40-80</th>
<th>$\gamma$ at 20 °C, 2 GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>N/A</td>
<td>N/A</td>
<td>0.033</td>
</tr>
<tr>
<td>H</td>
<td>0.0239</td>
<td>0.042</td>
<td>0.031</td>
</tr>
<tr>
<td>I</td>
<td>0.0246</td>
<td>0.0381</td>
<td>0.028</td>
</tr>
<tr>
<td>J</td>
<td>0.0288</td>
<td>0.0515</td>
<td>0.036</td>
</tr>
<tr>
<td>K</td>
<td>N/A</td>
<td>0.0459</td>
<td>0.037</td>
</tr>
<tr>
<td>L</td>
<td>0.024</td>
<td>0.0455</td>
<td>0.036</td>
</tr>
<tr>
<td>M</td>
<td>0.034</td>
<td>0.0676</td>
<td>0.039</td>
</tr>
</tbody>
</table>
4.4. Environmental properties

There are many ways to characterize a fluid from an environmental perspective. In this paper, biodegradability and the amount of renewable raw material have been considered. Biodegradability measurements were made according to standard methods OECD 301 B or F, see Table 8. The OECD adopted test guideline 301 “Ready Biodegradability” comprises six different methods, A to F. In this study, data based on method B, CO₂ Evolution Test (Modified Sturm) or F, Manometric Respirometry Test (oxygen consumption) have been used. The test result is presented as the relative biodegradation (%) over a specified time period. For readily biodegradable materials, the minimum result is 60% degradation over 28 days (with some additional constraints). The test methods are available from OECD [8].

The amount of renewable raw material varies according to the composition of each synthetic ester. Generally speaking, the polyol part is of petrochemical origin and thus non-renewable, whereas in most of the esters in this study, the fatty acid is of natural origin, i.e. renewable. For the calculation of the relative contribution of polyol and fatty acid to overall renewability (% renewable), the oxygen-to-carbonyl ester bond is "cut", and one oxygen atom per ester group is assigned to the polyol. The fatty acid fragment begins with the carbonyl fragment (carbon oxygen double bond).

5. Discussion

The α-value for the esters is low and stable as usual for esters. The reference fluid M has a high α-value, which is common for paraffinic hydrocarbons. The β-value is also low for all the esters and high for fluid M.

To be able to perform advanced EHD simulations, it is necessary to consider the pressure dependence of the properties. An example is when data for thermal conductivity at atmospheric pressure are used in an EHD calculation, this will underestimate the film thickness. This is because the fluid could better take care of the generated heat at higher pressure thus both thermal conductivity

### Table 7
Thermal conductivity and specific heat capacity for the tested fluids

<table>
<thead>
<tr>
<th></th>
<th>λ at 20 °C (W/m °C)</th>
<th>λ at 80 °C (W/m °C)</th>
<th>ρCₚ at 20 °C (MJ/m³ °C)</th>
<th>ρCₚ at 80 °C (MJ/m³ °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>0.160</td>
<td>0.155</td>
<td>1.78</td>
<td>1.90</td>
</tr>
<tr>
<td>H</td>
<td>0.162</td>
<td>0.162</td>
<td>1.80</td>
<td>1.80</td>
</tr>
<tr>
<td>I</td>
<td>0.170</td>
<td>0.160</td>
<td>1.83</td>
<td>1.90</td>
</tr>
<tr>
<td>J</td>
<td>0.142</td>
<td>0.135</td>
<td>1.79</td>
<td>1.88</td>
</tr>
<tr>
<td>K</td>
<td>0.143</td>
<td>0.140</td>
<td>1.79</td>
<td>1.85</td>
</tr>
<tr>
<td>L</td>
<td>0.142</td>
<td>0.140</td>
<td>1.85</td>
<td>1.92</td>
</tr>
<tr>
<td>M</td>
<td>0.130</td>
<td>0.125</td>
<td>1.73</td>
<td>1.80</td>
</tr>
</tbody>
</table>

Fig. 3. Thermal conductivity as a function of pressure up to 1 GPa at 20 °C.

### Table 8
Biodegradability and relative amount of renewable raw material

<table>
<thead>
<tr>
<th></th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
<th>K</th>
<th>L</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>86</td>
<td>66</td>
<td>89</td>
<td>84</td>
<td>83</td>
<td>18</td>
<td>0</td>
</tr>
<tr>
<td>Renewable OECD 301</td>
<td>80°</td>
<td>63</td>
<td>86</td>
<td>70</td>
<td>73.7</td>
<td>N/A</td>
<td>25°</td>
</tr>
</tbody>
</table>

* Estimated biodegradability.
and specific heat capacity increases in the high pressure EHD contact.

The EHD friction for a fluid is important in many applications thus it directly impacts the systems overall efficiency. If fluid I is chosen instead of fluid M for an application where EHD friction causes the major losses due to sliding, the power loss can be reduced up to one third.

The relative ease of biodegradation is highly dependent on the molecular structure of the ester. Chain length, chain branching and steric crowding all affect the rate of hydrolysis (which is the first step in biodegradation) and the subsequent metabolic pathways. The chemical structure varies within the group of esters, and so does the biodegradability. Vegetable oils are generally less hydrolytically stable and biodegrade to a higher extent (and more rapidly) than these synthetic esters in the test environment.

All the fluids in this study, except the reference mineral oil M, could be considered environmentally adapted to a considerable extent. All the esters, except the complex ester L, are based on renewable raw materials to a relatively high amount (66–86%), which may be considered to be advantageous for a sustainable development. The biodegradability is good–excellent for these esters, “readily biodegradable” as defined in OECD 301 B/F.

6. Conclusions

All the esters have high thermal conductivity and specific heat capacity in comparison with the mineral oil. There is a strong correlation between the number of carboxylate groups and the thermal conductivity. The thermal conductivity increases with increasing number of carboxylate groups. The PE oleate (fluid I) has the highest and the NPG based diesters (fluids J and K) have the lowest $\lambda$-value of the synthetic esters. The $\rho$C$_p$ plot in Fig. 4 shows some trace of phase transformations for some of the fluids (I and M). It is not possible to state this transition represents crystallization or the formation of a glassy phase.

The EHD friction coefficient varies relatively little for different fluids but as expected the paraffinic mineral oil (fluid M) has the highest value. The PE oleate (fluid I) has the lowest EHD friction. The friction value also seems to correlate to the number of carboxylate groups. If the fluid has many carboxylate groups the friction is decreased.

The best base fluid choice for an environmentally adapted lubricant (EAL) will depend on all demands facing the application in question. A trade-off between biodegradability, renewability and performance often has to be made, and the functional demands affecting, e.g. the application life time, should be considered over the entire life cycle.

Acknowledgements

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References

Paper C
FILM FORMATION CAPABILITY OF ENVIRONMENTALLY ADAPTED BASE FLUIDS

A. Pettersson, J. Lord and E. Kassfeldt
Luleå University of Technology, Division of Machine Elements, SE-971 87 Luleå, Sweden, e-mail: ap@mt.luth.se.

ABSTRACT
The film formation capabilities of six environmentally adapted ester based fluids have been investigated using optical interferometry in a Ball and Disc apparatus. A mineral oil was used as a reference. The properties and molecular structure for the tested base fluids are well known from earlier investigations. The fluids were tested at three different slide/roll ratios of 0, 0.6, and 1.2. The film formation capability was compared to the molecular structure and other properties. It was found that some of the fluids maintain a superior lubricating film at high slide/roll ratios than others, because of their molecular properties. A high level of carboxylate groups in the ester molecule gives high thermal conductivity and heat capacity, which promotes heat transportation out of the contact and this also maintain separation.

NOMENCLATURE
\( \alpha \) Pressure viscosity coefficient, [GPa]  
\( \eta \) Dynamic viscosity, [Pas]  
\( \eta_0 \) Dynamic viscosity at 40 °C, [Pas]  
\( \lambda \) Thermal conductivity, [W/m°C]  
\( \bar{\rho} \) Dimensionless density  
\( h \) Film thickness, [nm]  
\( H \) Dimensionless film thickness  
\( p \) Pressure [Pa]  
\( T \) Temperature  
\( u \) Mean speed \((u_b+u_d)/2\), [m/s]  
\( \beta \) Temperature viscosity coefficient  
\( \bar{\eta} \) Dimensionless viscosity  
\( \kappa \) Kinematic viscosity, [cSt]  
\( \lambda_0 \) Thermal conductivity at 40 °C, atm.p  
\( A_s \) Slide to roll ratio \((u_b-u_d)/(u_b+u_d)\)  
\( h_c \) Central film thickness, [nm]  
\( H_c \) Dimensionless central film thickness  
\( p_h \) Hertzian maximum pressure, [GPa]  
\( T_o \) Test temperature, 40 °C

Keywords: lubrication, environmentally adapted lubricants, EAL, Optical interferometry and Film thickness

1 INTRODUCTION
To understand a base fluid’s capability to form a lubricating film under elastohydrodynamic lubrication, its properties have to be well known. Highly important factors for film formation under EHL conditions are high viscosity and high viscosity- and pressure coefficients. Other parameters that influence the lubrication film are the temperature-viscosity coefficient (VI) and thermal conductivity. Film thicknesses can be accurately estimated when the contact is subjected to pure rolling, as shown by several authors (see e.g. [1-3]). Although bulk fluid properties are known, it is still generally difficult to estimate the thickness of the separating film when the contact’s condition is more severe, e.g. when sliding is introduced. Due to the increased shear rate at the inlet, molecules tend to align in the direction of shear, effectively reducing the apparent viscosity. In addition, the increased shearing promotes heat generation that further reduces viscosity. This combined effect causes the film thickness to decrease significantly. The difficulty in modeling these phenomena has increased the need to develop experimentally deduced factors to be incorporated in well-established film thickness formulas. Gupta et.al. [4] compiled a thermal correction factor based to the work of Cheng [5] and Wilson and Sheu [6]. Smeth and Spikes [7] later found that earlier work underestimated the decrease in film thickness due to sliding. Since this decrease is caused by thermal and non-Newtonian effects, it is reasonable to believe that the reduction is different between different fluids. Lord and Larsson [8] tested the amount of film thickness reduction due to sliding with three different types of base fluids and found that the reduction differed where the ester-type lost the least film thickness relative to a mineral and a poly-α-olefin.

In this study, the film formation capabilities of six esters and one mineral reference fluid are investigated for three different slide/roll ratios, including pure rolling. The main objective is to extend knowledge of the relationship between the molecular structure and the film formation capabilities of environmentally adapted synthetic esters.

2 TESTED FLUIDS
The various fluids chosen for investigation in this study are listed in Table 1. The molecular structures for some of the fluids are shown in Figure 1. All fluids are in the ISO VG 46 range of viscosity, except fluid 1, which is an ISO VG 68. The fluid suppliers provide information about the density at 15°C and the kinematic viscosity at 40 °C and 100 °C. A three letter notation was given to each fluid to simplify data processing and result presentation, see Table 1, last column. Bis-(2-ethyl-
hexyl) sebacate was chosen as calibration fluid for the viscosity measurements, since its viscosity-pressure relationship is well known [9]. The sebacate is a synthetic diester and is available in a highly pure form. The mineral (M) oil that is of a solvent neutral, paraffinic type is included as a reference. The properties of these fluids are known in detail from [10]. All tested fluids are suitable for formulation of environmentally adapted hydraulic fluids.

All the selected fluids are of ester type. Esters are normally used as lubricants and classified in three different groups, viz. diesters, polyol esters, and complex esters. In this investigation fluids G and H are synthetic polyol tri-esters based on the alcohol trimethylol propane (TMP), with ideally only oleic acid tails (C18:1). The IMP fluid (improved TMP oleate) is a modified TMP oleate. It is partly complexified with adipic acid, while some of the oleic acids are exchanged with shorter, saturated, fatty acids to keep its viscosity to ISO VG 46. It has better high temperature stability and better VI. The biodegradability according to OECD 301 B/F is slightly lower than for TMP oleate, though the fluid is still readily biodegradable. Fluid I, the PE oleate, is a tetra ester based on pentaerythriol and oleic acid tails (C18:1). Fluids J and K are diesters based on neopentylglycol (NPG) and various fatty acids. Fluid L is a complex ester based on 2-Ethyl-2-butyl-1, 3-propanediol, and sebacic and octanoic acids.

![Schematic molecular structure of fluids TMP, PEO, ISO and C16](image)

**Figure 1** Schematic molecular structure of fluids TMP, PEO, ISO and C16

**Table 1 Tested fluids**

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Trade name</th>
<th>Molecular formula</th>
<th>Notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>TMP oleate</td>
<td>C_{36}H_{61}O_6</td>
<td>P 2089</td>
</tr>
<tr>
<td>H</td>
<td>Improved TMP oleate</td>
<td>C_{36}H_{61}O_6</td>
<td>DP 5146</td>
</tr>
<tr>
<td>I</td>
<td>PE oleate</td>
<td>C_{36}H_{61}O_6</td>
<td>P 1445</td>
</tr>
<tr>
<td>J</td>
<td>NPG ISO C18</td>
<td>C_{36}H_{61}O_6</td>
<td>P 1973</td>
</tr>
<tr>
<td>K</td>
<td>NPG C16-C18</td>
<td>C_{36}H_{61}O_6</td>
<td>P 1923</td>
</tr>
<tr>
<td>L</td>
<td>Complex ester</td>
<td>N/A</td>
<td>DP 5148</td>
</tr>
<tr>
<td>M</td>
<td>Mineral oil</td>
<td>N/A</td>
<td>SN 215</td>
</tr>
</tbody>
</table>

**Table 2 Bulk fluid values ($\alpha$, $\lambda$, $\eta$ and $\beta$)**

<table>
<thead>
<tr>
<th></th>
<th>TMP</th>
<th>IMP</th>
<th>PEO</th>
<th>ISO</th>
<th>C16</th>
<th>CPX</th>
<th>MIN</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha \cdot 10^8$ [Pa$^{-1}$]</td>
<td>1.73</td>
<td>1.61</td>
<td>1.46</td>
<td>1.74</td>
<td>1.67</td>
<td>1.79</td>
<td>2.01</td>
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<tr>
<td>$\lambda_0$ [W/mK]</td>
<td>0.16</td>
<td>0.162</td>
<td>0.17</td>
<td>0.142</td>
<td>0.143</td>
<td>0.142</td>
<td>0.13</td>
</tr>
<tr>
<td>$\eta_0$ [mPas]</td>
<td>40.19</td>
<td>44.84</td>
<td>66.27</td>
<td>41.02</td>
<td>38.09</td>
<td>41.76</td>
<td>40.85</td>
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<tr>
<td>$\beta$ [K$^{-1}$]</td>
<td>0.0267</td>
<td>0.0274</td>
<td>0.0282</td>
<td>0.0334</td>
<td>0.0298</td>
<td>0.0276</td>
<td>0.0405</td>
</tr>
</tbody>
</table>
The bulk properties of the tested lubricants may be found in Table 2. The β value given is defined according to Eqn.1:

$$\beta = \frac{\ln \eta - \ln \eta_0}{T_0 - T}$$

where β represents a best fit to viscosity temperature data in the temperature range 40 °C-50 °C.

3 EXPERIMENTAL DETAILS

To determine the fluids' film forming capabilities, tests were carried out using a Ball & Disc apparatus [11]. In this rig, a highly polished steel ball is loaded against a transparent sapphire disc, while the contact is continuously fed with lubricant. The speeds of the ball and disc can be set independently as to create any condition of slide to roll ratio. By illuminating the ball and disc contact and simultaneously monitoring it through a microscope using a CCD-camera, images of the contact can be acquired. Since the disc is coated with a thin layer of chromium, the incident light generates optical interference that is captured and processed digitally for film thickness. The multi channel method was used to for this purpose [1].

All experiments were conducted at 40 °C ±0.5°C and the contacts were supplied with enough oil in order to avoid starvation. The speed was varied from a lower limit were the film thickness were approximately 100 nm up to 2.4 m/s. The lower limit is due to the minimum film thickness that can be measured using this specific setup. Thinner films may be measured with other setups, but this was not the scope for the current case. A constant load was chosen as to give a maximum Hertzian pressure of 1.13 GPa. Each fluid some subjected to 3 different tests with a varying slide to roll ratio, Ac, of 0, 0.6, and 1.2.

4 RESULTS

Results from the film thickness measurements are shown in Figure 2. Only the results from the worst sliding case A, = 1.2 and the pure rolling case A, = 0 are given. The plots have also been divided into two for clarity, but the results from the reference mineral oil are given in both. Both the mineral reference fluid (MIN) along with the PE-Oleate (PEO) has the thickest film for pure rolling. It should, however, be remembered that the PEO is a VG68, while all others are VG 46. The ISO forms a slightly thicker film than the IMP and the CPX. The thinnest is created by the TMP, even though the differences between the latter three are small. As expected, the film thickness decreases significantly when sliding is introduced. As shown in Fig. 2, the amount of film thickness reduction varies among the fluids, where it is relatively large for the MIN by comparison.

Figure 2 Film thickness from Ball and Disc measurements for A, = 0 and A, = 1.2. Two curves are shown for each fluid. The lower trace always describes the case of A, = 1.2.
Although the lubricants often have rather similar bulk properties it would be advantageous to reduce the effects of these during result interpretation. Lord et al. [8] formed a dimensionless film thickness parameter, shown in Eqn. 2, which enabled the results to show the inherent film forming properties of each lubricant apart from those used in the dimensional analysis.

\[ H = \frac{h}{\alpha} \left( \frac{\beta}{\eta_0 \lambda_0} \right) \]  

(2)

To reduce the interference of thermal effects, the non-dimensional film thickness \( H \) has been plotted against a thermal loading parameter \( Br \), i.e. the Brinkman number shown in Eqn. 3. It may be interpreted as the ratio between the heat developed to that which has dissipated away.

\[ Br = \frac{u^2 \eta \beta}{\lambda} \]  

(3)

It may be seen from Fig. 3a that the tested lubricants fall into two distinct categories under pure rolling conditions, i.e. fluids that are “mineral-like” and “ester-like”. When \( A_c = 0 \), the inlet shear rate is low; hence, this case is the closest to resemble an isothermal condition. Lord and Larsson [8] found that the fluids they tested all closely followed a single trace when these variables were plotted for the pure rolling case. This is obviously not the case here, though Lord and Larsson’s trace is very close to the top group in Fig 3a. The major differences between these experiments, apart from other fluids, are the much higher Hertzian pressures used in the current investigation, 1130 MPa compared to 464 MPa in [8]. This was accomplished by a higher load and a higher modulus sapphire disc. Since thermal and non-Newtonian effects are virtually non-significant under pure rolling, it is reasonable to believe that the deviating traces in Fig. 3a originate solely from the effects caused by the higher pressure.

Figure 3 Dimensionless film thickness as function of the Brinkman number for the three different slide to roll ratios a) \( A_c = 0 \), b) \( A_c = 0.6 \) and c) \( A_c = 1.2 \).
Table 3 Percentage film loss due to sliding at $Br = 0.04$.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Film loss, $A_e = 0.6$ [%]</th>
<th>Film loss, $A_e = 1.2$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIN</td>
<td>18</td>
<td>37</td>
</tr>
<tr>
<td>C16</td>
<td>19</td>
<td>38</td>
</tr>
<tr>
<td>ISO</td>
<td>16</td>
<td>33</td>
</tr>
<tr>
<td>TMP</td>
<td>12</td>
<td>29</td>
</tr>
<tr>
<td>IMP</td>
<td>13</td>
<td>31</td>
</tr>
<tr>
<td>PEO</td>
<td>16</td>
<td>25</td>
</tr>
<tr>
<td>CPX</td>
<td>15</td>
<td>32</td>
</tr>
</tbody>
</table>

For the nominally same input in pure rolling, the mineral reference oil, the ISO and the C16 gives approximately 18% higher $H$ than the fluids in the ester group. With an increasing amount of slide, the absolute difference decreases between these groups as the mineral-group is more sensitive to shear. The percentage loss in $H$ at $Br = 0.04$ is shown in Table 3. There are clear differences between the two groups. MIN, C16, and ISO decrease their film thickness more than the ester-like group. The general trend is clear, but the difference between the ester-type CPX and the mineral-type ISO is marginal.

Fig. 4 shows the non-dimensional film thickness profiles for the tested lubricants. Note that the abscissa is a spatial dimension, not the Brinkman number. The shape of the curves is rather similar, but some characteristics can be seen in the difference between central film thickness and the separation just upstream of the outlet constriction (at the pressure spike location). If this difference in separation is large, one can assume that the compressibility of the fluid is high. However, according to Fig. 4, this behavior does not differ appreciably between the fluids except for the CPX, which shows a stiff behavior resulting in a rather flat central zone. It is thus unlikely that compressibility is responsible for the deviation mentioned, though a numerical simulation was made to investigate its relation to $H$, as well as the pressure-viscosity coefficient.

Numerical simulations were made to investigate the relation between $H$ and compressibility as well as viscosity-pressure coefficients for MIN and TMP fluids. Since only qualitative results would suffice, a line contact simulation was made incorporating Roelands’ form of viscosity-pressure dependence (Eqn. 4) and Dowson-Higginson’s density-pressure relationship (Eqn. 5). Pressure-viscosity coefficient, $\alpha$, and the high pressure density asymptote, $a_{dpH}$, were varied. The maximum contact pressure was set to the current cases (1130 MPa and 464 MPa) and the calculations were made at $Br = 0.04$. The condensed results are shown in Table 4.

$$\eta = \exp\left(\frac{\ln(\eta_0) + 9.67}{-1 + \frac{p}{1.96 \cdot 10^8}}\right)$$

$$Z = \frac{1.96 \cdot 10^8 \alpha}{\ln(\eta_0) + 9.67}$$

$$\rho = \frac{0.59 \cdot 10^9 + a_{dpH} \cdot p}{0.59 \cdot 10^9 + p}$$

Where $a_{dpH}$ is the density asymptote corresponding to the maximum compressibility at infinite pressure. The mineral oil value for $a_{dpH}$ is a standard value 1.34. The value for the ester was set to 1.44, according to the results from Höglund [12], who states an $a_{ml}$ value of 1.40. A higher value was used to exaggerate possible effects.

From the results given in Table 4, it is clear from the small difference in $H$ that the compressibility and density changes cannot fully explain why the $H$-$Br$ traces diverge at higher pressures. A possible explanation may thus be that the mineral-like fluids’ (MIN, ISO, and C16) ability to keep their film forming capability at elevated pressure is due to the transformation to a glassy phase in the inlet at pressures over 700 MPa. Ester-like fluids (TMP, IMP, PEO, and CPX) do not easily become glassy at higher pressure; hence, the effective viscosity does not increase as much.

Table 4 Varied model parameters and calculated film thickness.

<table>
<thead>
<tr>
<th>$p$ [MPa]</th>
<th>$\alpha$ [GPa$^{-1}$]</th>
<th>$a_{dpH}$</th>
<th>$H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>464</td>
<td>20.1</td>
<td>1.34</td>
<td>73.4</td>
</tr>
<tr>
<td>464</td>
<td>17</td>
<td>1.44</td>
<td>68.4</td>
</tr>
<tr>
<td>1130</td>
<td>20.1</td>
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<td>64.8</td>
</tr>
<tr>
<td>1130</td>
<td>17</td>
<td>1.44</td>
<td>59.1</td>
</tr>
</tbody>
</table>

If solidification is the main reason for the mineral group to retain its film thickness when the Hertzian pressure is increased (from 464 to 1130 MPa), it is interesting to note that the relative decrease in separation (Table 3) is large when slide is applied.
Because of the branching of the fatty acid chain, the ISO fluid is more resistant to solidification than the C16 fluid. Resistance against solidification can be seen in Figure 3 where the ISO fluid is closer to the other esters in the lower group. Branching also affects the pour point that is lower than for the C16 fluid. It also shows a lower film loss in Table 3 than the C16 fluid.

PEO fluid could maintain a better lubricating film than the other fluids under severe sliding conditions through high thermal conductivity and high specific heat capacity. The high thermal conductivity comes from fluid that has a high level of carboxylate groups. A high level of carboxylate groups also gives a low transient friction coefficient that is beneficial for low heat generation under sliding conditions.

5 CONCLUSIONS
The main aim for the present work was to investigate whether ester based fluids subjected to high pressures and shearing could compete with a mineral oil in forming a separating film. Of six tested esters, two (ISO, C16) are directly comparable with the mineral. In general, these fluids possess similar bulk properties to the mineral, causing similar behaviour in high shear film loss. ISO and C16 are thus mineral like under the tested conditions, but have the advantage of being readily degradable.

Esters (TMP, IMP, PEO, and CPX) not having the mineral like properties of C16 and ISO, show less ability to form a thick film under near iso-thermal conditions. Instead, these fluids are better at retaining the film as the degree of sliding increases. As a result, esters cannot be treated as a group where all have a similar behaviour. The application must then set the conditions to which ester is suitable, film formation or film thickness shear stability.

The mineral like fluids used in the investigation are less sensitive to increased Hertzian pressure on film thickness. The suggested reason is the formation of a glassy phase. Less pressure dependent esters that do not easily solidify reduce the film thickness accordingly.

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7 REFERENCES