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Tribology for Greener Combustion Engines

Scuffing in Marine Engines and a Lubricating Boric Acid Fuel Additive

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Abstract
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This thesis aims at increased knowledge in two fields of tribological research; both related to making currently used combustion engines greener. The first field regards the possibilities of using a boric acid fuel additive to increase fuel efficiency. The second field is about the severe wear phenomenon scuffing, which can become problematic when cargo ships are operated on low-sulphur fuel to reduce sulphuric emissions.

Tribological tests were developed and performed to simulate the applications. Advanced surface analysis was performed to understand changes occurring on the outermost surface of sliding components, which affect friction and wear. Samples from engines were studied to verify the relation between the lab tests and the applications.

In the case of boric acid, the coefficient of friction was below 0.02 for large parts of the tests, but varied with test parameters. The corresponding reduction in friction was up to 78% compared with tests without the additive. As an attempt to assess if the substantial fuel savings found in field tests with passenger cars (6%) can be explained by friction reduction in boundary and mixed lubricated parts of the piston assembly, assumptions were presented that would lead to fuel savings close to these 6%. Boric acid was detected on surfaces after the tests, and the tribofilm appearance depended on test parameters. The tribofilms were shown to be affected by storage time and test temperature; a finding that is vital for future studies.

In the case of scuffing, mechanisms were studied and accumulation of wear debris had a significant role on scuffing initiation in the lab scale scuffing tests. Regarding the possibility to test materials scuffing resistance, there was a large scatter in the results, and thereby difficult to draw conclusions. Two new piston ring materials were identified to perform somewhat better than the currently used.

In conclusion, findings that could facilitate immediate improvement of fuel efficiency of today's combustion engine vehicles as well as findings that strengthen available hypotheses on scuffing mechanisms are presented. The latter offers improved understanding of scuffing and thereby give possibilities to counteract the higher risk associated with operation on cleaner fuel.

Keywords: Friction, wear, lubrication, energy loss, atmospheric emissions, fuel efficiency, transport.

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Om vi inte kunde skratta så skulle vi ha gett upp alltsammans för länge sedan

Elin Wägner

List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

I Larsson, E., Olander, P., Jacobson, S. (2017) Boric acid as a lubricating fuel additive. Simplified lab experiments to understand fuel consumption reduction in field test. *Wear*, 376-377:822–830.

II Larsson, E., Olander, P., Jacobson, S. (2017) Boric acid as a fuel additive. Friction experiments and reflections around its effect on fuel saving. *In manuscript*

III Olander, P., Hollman, P., Jacobson, S. (2013) Piston ring and cylinder liner wear aggravation caused by transition to greener ship transports. Comparison of samples from test rig and field. *Wear*, 302:1345–1350

IV Olander, P., Eskildsen, S.S., Fogh, J.W., Hollman, P., Jacobson, S. (2014) Testing scuffing resistance of materials for marine 2-stroke engines. Difficulties with lab scale testing of a complex phenomenon. *Wear*, 1340-341:9–18

V Olander, P., Jacobson, S. (2015) Scuffing resistance testing of piston ring materials for marine two-stroke diesel engines and mapping of the operating mechanisms. *Wear*, 330-331:42–48

Author’s contributions to the papers

Paper I	Part of planning, experimental work, evaluation and writing
Paper II	Large part of planning, evaluation and writing
Paper III-V	Major part of planning, all of experimental work, major part of evaluation and writing

Contents

Abbreviations

ASTM	American Society for Testing and Materials
BL	Boundary lubrication
CVD	Chemical vapour deposition
DLC	Diamond like carbon
EDS	Electron dispersive X-ray spectroscopy
EHD	Elastohydrodynamic
EHDS	Elastohydrodynamic sliding
EP-additive	Extreme pressure additive
HD	Hydrodynamic
HFO	Heavy fuel oil
HVOF	High-velocity-oxygen-fuel
IC engine	Internal combustion engine
ML	Mixed lubrication
PAO	Poly-alpha-olefin
PS	Plasma sprayed
PVD	Physical vapour deposition
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
vol%	Volume percentage
wt%	Weight percentage
XPS	X-ray photoelectron spectroscopy
ZDDP	Zinc dialkyldithiophospate

1 Introduction

Tribology and environment, two words interweaved into this thesis. But what is tribology and how is it connected to our environment?

I will start with our frame; the environment of planet earth is the framework where we live, love, grieve and worry. This environment is ever changing and during the relatively stable 11,700-year-long period called the *Holocene epoch*, development of the human societies of today has been enabled [1]. Advances in farming, technology and medicine are some of the foundations of modern global societies. But the extreme progress during the last centuries has not only led to positive outcomes; it has also influenced our environment negatively. One of the first to bring up environmental concerns to the general public was Rachel Carson, an American marine biologist. In 1962, she explained the wider perspective of the use of DDT and its effect on wildlife in her famous book *Silent Spring* [2]. Since then, both local and global environmental alarms have become part of our everyday lives. Locally, *acid rain* originating from industries and sea transports is harmful for human health, destroys cultural heritage and reduces biological diversity of lakes. Globally, emission of carbon based *greenhouse gases* to our atmosphere are causing amplification of the greenhouse effect, leading to global warming. This man-made climate change threatens the stability of our environment and thereby our societies [1]. Acid rain and global warming are two out of many environmental concerns on earth today. The possibility to reduce these problems with the help of tribology is the focus of this thesis.

The term tribology is derived from the Greek words for rubbing and "study/knowledge of", tribos and logia. Tribology is the science of interacting surfaces in relative motion, the science of friction, wear and lubrication. Tribology can be considered as a multidisciplinary field of science, including physics, chemistry, mechanics, thermodynamics and material science.

The concept of tribology is not new. Thousands of years ago, sledges used to move heavy rocks to the Pyramids in the ancient Egypt were lubricated with water. Later, 500 years ago Leonardo da Vinci studied basic friction mechanisms. However, the first time the term tribology was used was only 50 years ago in the famous Jost report [3]. In this report, it was estimated that potentially £5000 million per year could be saved with tribological improvements only in the UK. Part of this, £28 million, was directly from reductions in energy consumption through decreased friction. This was before most people knew anything about the environmental aspects of using fossil fuel energy, but lately, tribological research has often been devoted to solving environmental problems. Reduction of energy losses in transports, strongly linked to reductions of emitted greenhouse gases, is one example. About 28% of the fuel in a car is lost in direct frictional losses, which means that about 208 000 million litres of fuel is used to overcome friction in cars every year [4]. Consequently, many researchers and engineers are working on reducing these energy losses, often with the help of advanced material research and high-resolution electron microscopy to enable increased understanding of the optimal tribological performance.

Tribological research is also focusing on reducing *wear* of sliding materials. This gives higher quality and longer service life of components, but also savings of raw materials. Reduced wear can thereby lead to secondary energy savings, since energy is required for extracting and refining raw materials. Further, changes needed for environmental improvements can also cause tribological problems that need to be dealt with. Examples of such changes include removal of harmful compounds such as sulphur from fuel, and lead from gasoline as well as from bearings.

There is no doubt that tribological research and other new technology can contribute to a lower environmental impact per travelled kilometre or transported freight. But it is also important to consider whether technical solutions alone can help humanity to stay within the sustainable boundaries of our planet. By reviewing literature on greening of passenger transports, Moriarty et al. showed that it is not likely that technical solutions by themselves can lead to the needed reductions in greenhouse gas emissions [5]. Reducing the transport task in general is as important to counteract effects from economical growth and development. The so-called *rebound effect* can otherwise lead to increased emissions. The rebound is a measure of the extent of an expected energy saving that is reduced due to the subsequent higher use or other types of effects. As an example, a more fuel-efficient engine in a passenger car can lead to lower travel costs. This can lead to extra driving or to increases in general consumption and thereby to increases in energy usage due to increased production and transports. This realisation has its roots back to the 19th century English economist William Stanley Jevon (*Jevon's paradox*). Later on, in the 1980's, Brookes and Khazzoom independently presented observations where higher energy efficiency tends to lead to an increase in energy use rather than a decrease [6, 7] (see *Figure 1*). Basic mechanisms of rebound are widely accepted, but the magnitude is debated in economical literature [8]. Yet, many researchers are stressing the importance of policies to reduce the pressure on resources in total, for instance regarding passenger transport [5] and global consumption patterns [9].

In other words, too much focus on technical solutions can direct attention away from other approaches necessary for staying within our only known framework for modern life. Nevertheless, technological improvements are important steps forward, and are of course the focus of this technical thesis.

Figure 1. Without a huge technological step change, the expected increase of car usage will lead to increased emissions of greenhouse gases even with incremental fuel saving improvements, including tribological approaches. The rebound effect can even lead to higher total consumption of fuel after the technological improvements.

1.1 Research objectives

This thesis aims towards improved knowledge in two fields of tribological research, both targeting greener combustion engines. Firstly, focus is directed on an increased understanding of the effects and possibilities of boric acid as a lubricating fuel additive (**Paper I and II**). This is one possible solution that could enable immediate reduction of energy losses in combustion engines. Secondly, focus is on a better understanding of *scuffing* and testing the scuffing resistance of sliding materials. (**Paper III, IV and V**). Scuffing is a catastrophic type of wear associated with poor lubrication. There are concerns for a higher risk of scuffing when cargo vessels are operated on cleaner fuel to decrease sulphuric emissions. The mechanisms behind scuffing have been studied for decades, but are still not well understood. Increased knowledge could facilitate the choice of preventive measures to counteract scuffing and thereby prevent problems caused by operation on cleaner fuel.

The work consists of five scientific papers and introductory chapters aimed towards the reader who wishes to get a broader background and state of the art insights into these fields of research as well as a summary of the papers.

2 Tribology in power cylinder of internal combustion engine

2.1 Internal combustion engines

Internal combustion engines (IC-engines) transform intrinsic chemical energy in fuels into mechanical energy used to power vehicles; they have been used to an ever-increasing extent since the first commercial engines in the middle of the 19th century.

Combustion of the fuel leads to increased temperature and pressure of compressed gases in the combustion chamber inside the engine. The resulting expansion force is doing work by pushing a reciprocating piston downwards in a cylinder bore, thereby giving it kinetic energy (IC-engines working with other mechanisms than pistons exist, but are not as widespread and not in focus here). The moving piston, often one of several pistons in a motor block, is attached to and rotates a crankshaft connected to for instance wheels of a vehicle, the propeller of a ship or an electrical generator (see *Figure 2*).

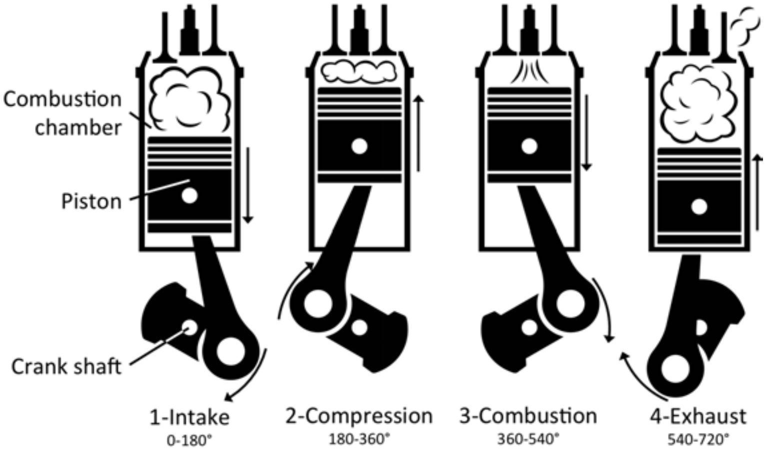


Figure 2. Basic principles of internal combustion engines: 1- intake of air, 2-compression of air, 3-raising of temperature by combustion and extraction of work from expansion of heated gases and 4 - exhaustion of gases. Here, the four-stroke principle is shown in one cylinder. Each combustion cycle consists of 4 strokes (down-up-down-up) and results in two crankshaft revolutions, hence 720°.

The most common types of IC-engines are *four-stroke* engines and *two-stroke* engines, where the main difference is how many strokes that are used for the characteristic features of the engine: 1) intake of air, 2) compression of air, 3) raising of temperature by combustion and extraction of work from expansion of heated gases, and 4) exhaustion of gases (see *Figure 2*). In *Figure 3*, an engine of the larger size is shown.

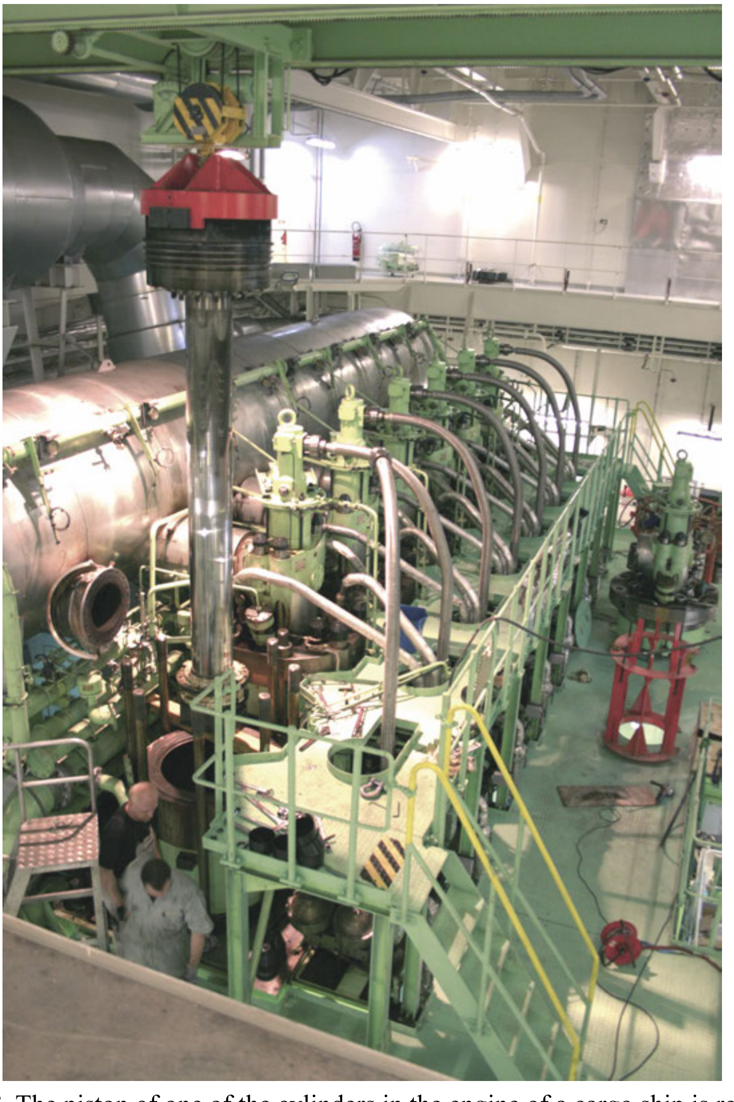


Figure 3. The piston of one of the cylinders in the engine of a cargo ship is removed for inspection of the piston rings and cylinder wall (Results are summarised in section 5.2). This is a two-stroke diesel engine with 7 cylinders, each with a displacement volume of 1300 litres, which can be compared with total displacements of about 2 litres in an engine of a passenger car and 14 in a truck engine.

Both four-stroke and two-stroke engines can work by one out of two principles for how the combustion process is started. In a *spark-ignition* engine, also called an *Otto-engine*, a spark ignites the fuel vapour; while in a *compression-ignition* engine, also called a *diesel engine*, the fuel is self-ignited due to high temperature caused by the high pressure. The previous is often fuelled with gasoline, while the latter, as the name suggests, is often fuelled with diesel. Other types of fuel can be used with both ignition-principles, for instance the heavy fuel oil commonly used in the two-stroke diesel engines in cargo-ships, and its potential replacement – natural gas.

Different types of engines are optimal for different applications. Four-stroke engines are in general used in automotive applications. Two-stroke spark ignition is instead used in small boats and motorcycles, where low weight is important. Two-stroke compression ignition on the other hand is used in low-speed marine applications due to their high energy-efficiency.

There are several sliding contacts in an IC-engine, for instance in piston assemblies, valve trains and crankshaft bearings. The *piston assembly* comprises sliding between the cylinder walls and the reciprocating piston (piston-rings and piston skirt) and also sliding between the piston pin and the piston bore. Sliding between piston-ring and cylinder wall is often said to be the largest contributor to frictional energy losses [4, 10, 11], and it is also the contact where the wear problem called scuffing sometimes occur in the marine low speed, two-stroke engines. Due to these reasons, this is the contact in focus of this thesis, and it will be described further in the next section.

2.2 Piston-ring/cylinder-wall contact

A piston ring is in principle a dynamic seal as it slides against the wall of the cylinder bore. Its main function is to seal off the pressure of the combustion gases so that the pressure is used to do work on the piston instead of causing blow-by of gases past the piston. To keep friction and wear low, the seal is lubricated. This imposes another function of the rings: to distribute enough oil for lubrication. At the same time they should control that excessive oil does not remain on the walls since this leads to high oil consumption due to evaporation and combustion. Additionally, the rings transfer heat from the piston to the liner and stabilises the piston in the cylinder bore.

Piston rings have a free diameter that is larger than the diameter of the cylinder bore. This implies that when the ring is fitted in its groove on the piston, the spring force caused by its own elasticity presses the ring against the liner. Rings and piston grooves are also designed so that the pressure of the combustion gases can act on the backside of the rings, hence increasing the sealing force further (see *Figure 4*).

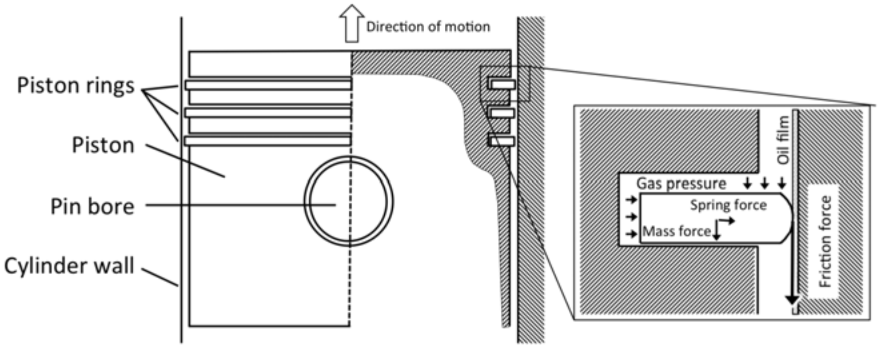


Figure 4. Schematic of piston in cylinder liner (right part in cross-section). Inset to the right: cross-section of piston ring in piston ring groove with forces that act on the ring (force arrows are not to scale).

2.2.1 Materials of piston-rings and cylinder wall

Piston rings are usually made of cast iron or steel [12], often with a coating to decrease friction and wear. The number of piston rings in a ring pack varies between different types of engines, usually 2-4 so-called compression rings and 0-3 oil control rings [13]. A diversity of cross-sectional geometries also exists. In the doctoral thesis by Rehl, the influence of ring geometry is shown to influence the friction behaviour [14]. Types of rings and ring designs are well described by Andersson et al. [13].

The bores of the engine block are often lined with a *cylinder liner*. Hence, this is the component in contact with the piston rings. The use of liners enables easier repair or exchange of the bore surface. The bore/liner surface is often made of Al-Si-alloys in spark ignition engines, and grey cast iron in compression ignition engines [14]. Al-Si-alloys have become popular due to their low weight, but are sometimes coated with plasma sprayed coatings to increase their wear resistance.

The surfaces of most bores/cylinder liners nowadays are machined with a process called *plateau honing* where a crosshatch pattern of grooves is formed by abrasive stones followed by flattening of ridges, which lead to formations of plateaus between the grooves. The cross-hatch pattern is believed to affect lubrication positively by retaining and distributing oil as well as by retaining wear debris [15, 16]. There is also research showing that the sub-surface structure formed during the plateau honing is optimal for low friction and wear [14, 17].

2.2.2 Lubrication

Engine oil is used to reduce friction and wear, to distribute heat and pressure and to remove wear debris from the sliding contact. Historically, lubrication occurred by the splashing by the rotating crankshaft in the crankcase oil. Now, a specially designed oil control ring is often used to help distribute a proper lubricant film and to scrape off excessive amounts of oil. This is the case in most four-stroke engines, while most small two-stroke engines are lubricated by oil in the fuel. In the large marine engines in focus of section 5, oil is sprayed onto the piston from the cylinder walls.

The dynamics of the piston and its ring is more intricate than the reciprocating motion up and down in the cylinder [18]. It is useful to keep this in mind when considering the lubrication situation. The piston is subjected to secondary motions (tilting and sideway motions, so-called piston slapping) in the cylinder as a result of the connection to the crank shaft (see *Figure 2*). This is sometimes avoided by the use of a so-called cross-head. Additionally, the rings can move up and down in their grooves (flapping) and can become twisted. To further complicate the picture, the clamping of the cylinder liner as well as gas forces and temperature gradients during operation lead to distortion of the cylindrical shape of the bore.

2.2.3 Lubrication regimes

There are two general mechanisms of friction reduction by lubricants: *boundary lubrication* and *full film lubrication.* These two mechanisms, and a mixture between them are known as lubrication regimes (see *Figure 5*. All these regimes can exist in the piston-ring/cylinder contact. The large variation in sliding speed, load and oil viscosity (a function of variations in temperature) during the strokes are some of the parameters that influence which mode of lubrication that is present at a specific location at a given moment.

In the *full film lubrication* regime, the pressure in the lubricant is high enough to separate the surfaces and the resulting friction force is the force needed to shear the oil film. In the piston-ring/cylinder liner contact, the relative motion of the rings creates the pressure in the lubricant. Such full film lubrication is called *hydrodynamic* (HD) lubrication.

The surfaces are irregular at micro-level and surface asperities are protruding out into the lubricant. When the HD film is thin, asperities from both surfaces will stochastically approach each other and come into contact. Momentarily, high local pressures can lead to elastic deformation of the asperities and consequently to local increase in viscosity of the oil. The localised elastic deformation together with increased viscosity lead to higher local film thickness than what is predicted by classical rheological calculations. This is called *micro-elastohydrodynamic* (micro-EHD) lubrication [19].

If the pressure in the lubricant is not high enough to separate the surfaces completely, some of surface asperities will come into contact with each other, while part of the load is still supported by the fluid pressure. This is the *mixed lubrication* (ML) regime and the overall friction force will come both from shearing of the oil and from shearing of the more or less solid surface films on the asperities.

In the *boundary lubrication* (BL) regime, a major part of the load is held by the asperities, and consequently, most of the friction force is coming from shearing within or between different types of surface films. The shearing can take place as sliding between molecules adsorbed on the surfaces, such as friction modifiers or within polymerized oil, so-called friction polymer [20, 21] or within the outermost solid material of the component. This is not the same as dry sliding, since the lubricant affects the outermost surface.

Knowledge about when and where each lubrication regime dominates is useful, whether it is to reduce fuel consumption by targeting friction losses or if it is to make the engine more reliable by increasing the scuffing resistance. The current understanding of breakdown between lubrication mechanisms is further discussed in section 4.3.4.

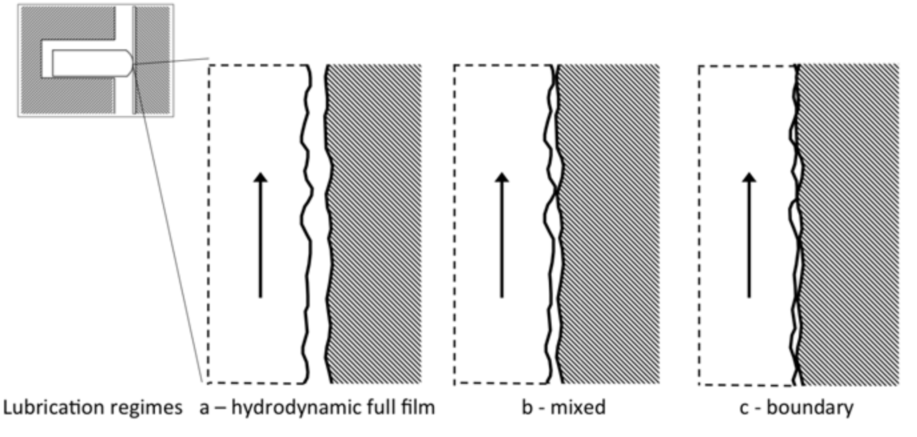


Figure 5. The three modes of lubrication: a) Hydrodynamic full film lubrication, b) mixed lubrication and c) boundary lubrication.

2.2.4 Friction in the piston-ring/cylinder contact

Friction can be considered as energy conversion and energy dissipation. The kinetic energy that is lost due to friction is mainly converted into heat that is conducted away, but also results in vibration and emission of sound, both leading to dissipation of energy. Some of the energy is converted within the material surfaces and wear debris by plastic deformation, material intermixing and tribochemical reactions (further discussed in section 2.2.5).

The friction forces, and thereby the frictional energy losses in the ring/liner contact will vary during the strokes (see Equation 1 and *Figure 6)*, since it is a product of the normal force (affected by the dynamic chamber pressure) and the coefficient of friction (affected by several factors including the mode of lubrication and properties of the near surface material).

Frictional energy loss = Friction force x Distance
= Coefficient of friction x Normal force x Distance Eq. 1

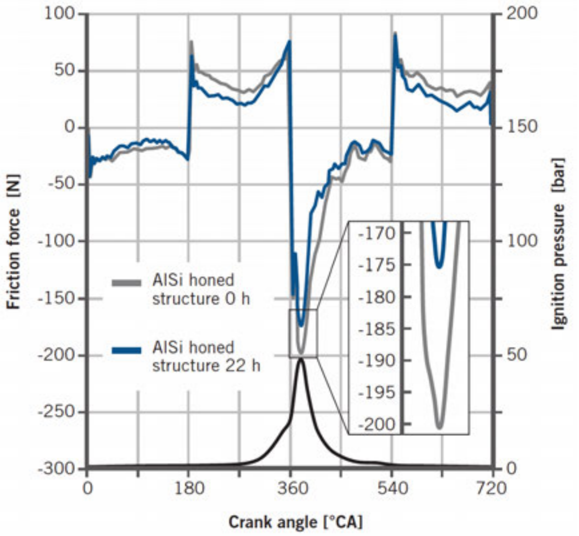


Figure 6. Example of result from a friction measurement in a fired single cylinder gasoline powered engine (floating liner technique. Blue and grey curve show friction force as function of crank angle, black curve show chamber pressure. The friction force has changed during running-in, i.e. between 0 and 22 h of running [22]. Reproduced with permission.

The *Stribeck-curve* is often used to qualitatively illustrate how the coefficient of friction is changed as a function of viscosity, sliding velocity and load (see *Figure 7*). The Stribeck-curve was originally describing the friction behaviour in journal bearings (see The Stribeck memorial lecture by Bo Jacobson [23]), but as its shape is based on common friction behaviour in BL, HD lubrication and the mix of these, it is generally used to describe the friction behaviour of various components, including the piston rings.

However, the contact between piston rings and cylinder liner in a firing engine is more intricate than in a journal bearing [12]. Apart from the fact that the speed, load and viscosity are dynamic and change rapidly, other parameters, including piston ring shape[14], surface topography, oil availability [24], secondary motions of the piston and piston rings [18], ignition timing [14] and properties of the surface layers [22] will affect the mode of lubrication and the friction level. Additionally, the surface topography and properties of surface layers are not constant parameters, but will depend on the history of the contact, such as preceding chemical environment and the running-in parameters [25]. This is discussed further in section 2.2.5.

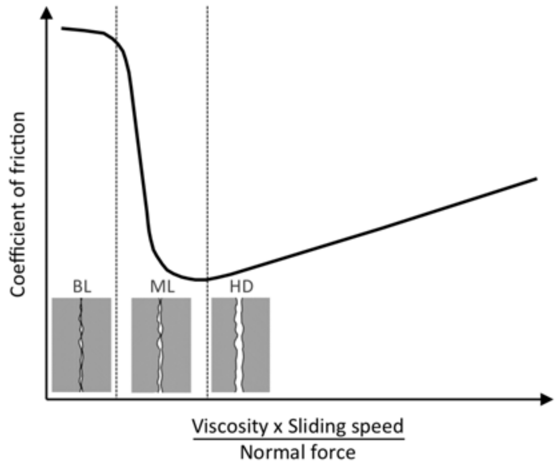


Figure 7. The Stribeck curve illustrates the general friction behaviour as a function of viscosity, sliding speed and normal force.

The Stribeck curve should be seen as a theoretical model that is valid in many cases, but not always. In a review paper by Andersson et al. [13], they state that several authors have shown results that do not follow the theoretical trend of the Stribeck curve. One example is the so-called inverse Stribeck curve behaviour observed when diamond like carbon (DLC) coatings are used [26]. Instead of a continuous increase in coefficient of friction when moving from ML towards BL, the friction is reduced at high loads.

2.2.5 Wear and surface changes

The wear rate in the piston ring/cylinder-wall contact is generally in the range of nm/hour, which is considered as very low [25, 27, 28]. For a passenger car at 1500 rpm, there will be 90 000 passages in each direction every hour, which means that the wear rate must be much lower than an atomic layer per passage.

The ultra-low wear rate is sometimes, especially in earlier literature, explained by the presence of full film lubrication, which separates the surfaces [29]. However, new wear theories have come up during the last decades that could explain the low wear even if asperities are in contact. Scherge and coworkers has in a series of publications studied the ultra-low wear rate present in the piston-ring/cylinder contact [25, 27, 28, 30]. They have used the *ra-*

dio-nuclide-technique [31], which allows measurement of ultra-low wear rate, combined with high-resolution electron microscopy (see *Figure 8)* for example of result obtained with the radio nuclide technique). They ascribe the ultra-low wear rate to the formation of an optimal surface layer that they call the third body (a term first used by Godet [32]). In their model, asperities are frequently transformed into a fluid-like state due to high local forces [33]. This leads to mechanical intermixing of entire asperities and introduction of elements from the surroundings and thereby to formation of new material (i.e. lubricant, combustion by-products, counter surface and atmosphere). As this occurs at thousands of asperities the outermost surface layer is gradually modified in terms of crystallinity, morphology and chemical composition. A thin (10-100 nm) soft nano-crystalline top layer is formed on the surface, where the high level of grain boundaries determines the mechanical properties. Underneath, there is a deformation hardened layer.

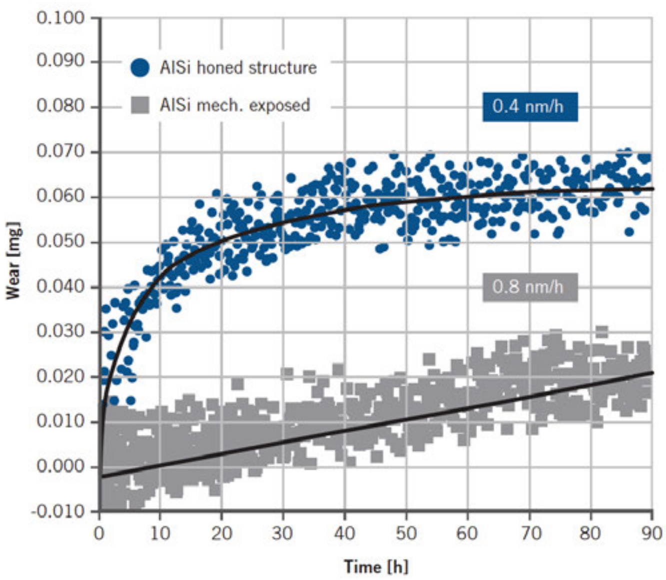


Figure 8. Accumulated wear as function of running time. Wear data is obtained with the radionuclide technique, Here, the wear rate of a sample representing a cylinder liner in a simplified component test, but the technique is also used in engine tests. The blue and grey curve show wear behaviour for cylinder liners processed with different surface preparation techniques. Although the honed surface (blue dots), has a higher initial wear rate, the steady state wear rate 0.4 nm/h is lower than the steady state wear rate of the so-called mechanically exposed surface (grey squares). If these wear rates continue, the accumulated wear will eventually become higher for the mechanically exposed surface [22]. Reproduced with permission.

Even at very low wear rates, there are significant plastic deformation and modifications of the surface layer. Popov has presented simulations based on so-called movable cellular automata where these types of layers resemble turbulent flow of the micro contacts [34, 35]. The wear mechanisms of this ultra-low wear is described as a squeezing process, where wear debris stochastically are detached and remixed into the surface or transported out of the friction zone. After repeated inclusions and squeezing, wear particles leave the nominal contact.

Examples of these types of layers are shown in *Figures 9 and 10*. *9* show a cross-section in the sliding direction of a grey iron cylinder liner removed from a marine two-stroke diesel engine. Grain refinement is visible close to the surface. To the right, a plastically deformed tongue appears to have become pushed down into the surface. *Figure 10a* shows a transmission electron microscopy (TEM) image of a cross-section in sliding direction from a steel sample tested in a lubricated pin-on-disc test. The outermost layer is nanocrystalline, which is shown in *Figure 10b* (red circle in *Figure 10a*) and the associated diffraction pattern in *Figure 10c*. A base oil without additives was used (poly-alpha-olefin), meaning that chemical reactions and build up of new material is restricted to that of carbon, hydrogen and oxygen.

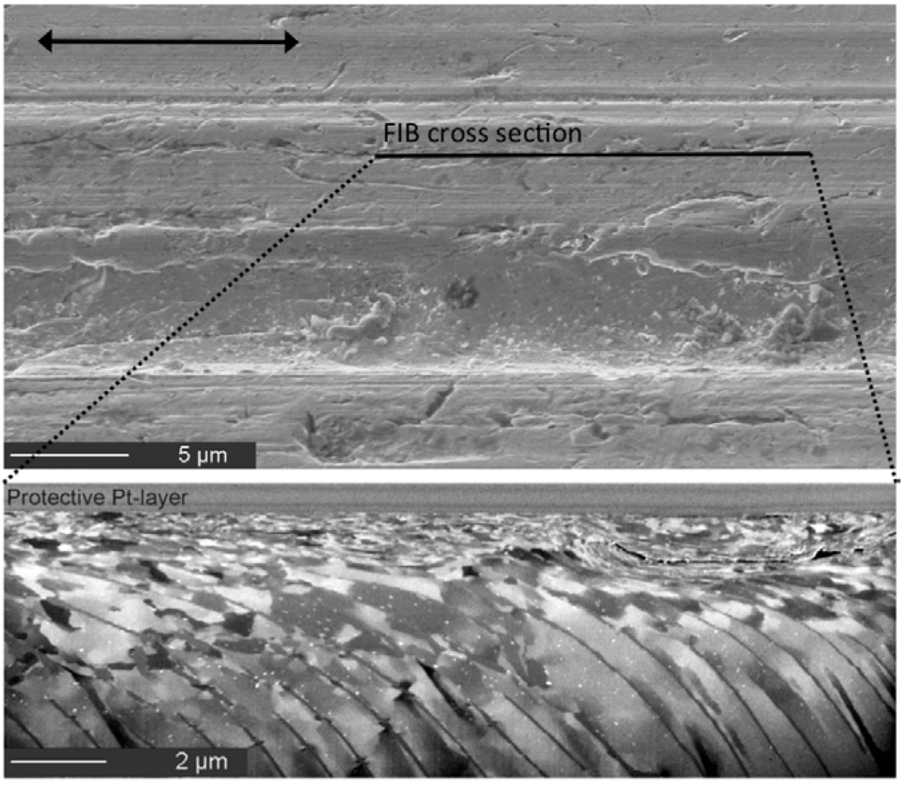


Figure 9. Focused ion beam (FIB) cross-section in the sliding direction of a cylinder liner removed from a well-running marine two-stroke diesel engine. The position of the cross section is marked in the upper image. In the lower part, a secondary ion image of the cross section shows strong shearing of the original grain structure, and a superficial layer with sever deformation and grain refinement. SEM.

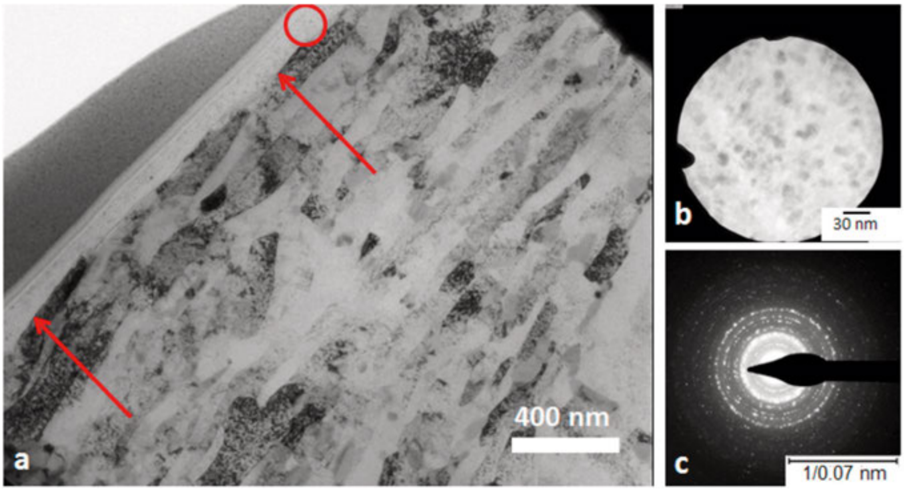


Figure 10. a) Cross section in the sliding direction of a steel disc sample from a lubricated pin-on-disc test lubricated with base oil, a) TEM image and c) diffraction pattern from the area in the red circle (and 7b) [30]. Reproduced with permission.

Factors leading to optimal surface properties

The most interesting part of the wear model presented by Scherge and co-workers is perhaps that the running-in conditions must be "just right" for an optimal third body to be formed and an optimal steady-state ultra-low wear rate to be obtained [17]. These optimal conditions are called the *running-in corridor*. The energy input must be high enough to initiate plastic flow and mechanical intermixing. If the running-in conditions are too mild, the power is not high enough to "ignite the necessary mechano-chemical reactions to form the third-body" [30]. Although a constant wear rate is obtained, it is higher than after the harsher, but optimal running-in conditions. If instead the conditions are too severe, the initial wear rate becomes too high to enable formation of an optimal third body.

In addition to the running-in conditions, the preceding surface preparation can also give the right energy input and thereby aid low friction and wear [22, 30].

Compounds from the surrounding will be mixed into and/or chemically react with the surface. Hence, additives and other compounds in fuel and cylinder oil can affect the properties of the modified surface. The sliding materials of both surfaces will also influence the properties of the modified layer.

Surface changes in various applications

The concept presented by Scherge and co-workers, directly builds on work of others, such as Rigney [36, 37], but is new in the way it explains the low friction and wear in lubricated contacts in engines. It means that full film lubrication must not be the sole explanation for ultra-low wear rate. However, the fact that the outermost surface layer is modified during tribological contact and differs from the original surface as well as from the bulk material is not a new concept. It has been described in several different applications. Beilby was probably the first to describe this phenomenon, sometimes called the *Beilby layer* [38]. In his book published in 1921, where 20 years of research was summarized, he writes:

> The polished surface is formed by true skin (...) it possesses distinctive qualities which differentiate its substance very clearly from that of the unaltered substance beneath it

A more recent example is that of *Stellites* (Co-Cr alloys), where the surfaces during high loading transform into a thick deformation hardened layer with an easily sheared layer of atomic planes aligned with the surface [39]. Another example is that of a tribochemically active TiC/a-C-coating with incorporated sulphur [40]. The added sulphur lowers the friction in contacts against steel, but has an even higher effect in contact with tungsten, where a lubricating WS_2 layer is formed in the tribological contact.

The complex and versatile nature of tribologically induced surface modifications within different applications has lead to many names for these phenomena [41], including transfer films, built-up layers, tribolayers, tribosintered layers, tribofilms, selective transfer layer and self-organising surface films. In their overview of tribologically modified surface layers, Jacobson and Hogmark chose to apply the term tribofilm in all cases [41]. This term is commonly used by some [42, 43], while others find that it sounds too much like if a film is formed upon the original surface rather than a transformation of it, and thereby prefer the term third body [17].

In the papers of this thesis, the term tribofilm is used for surfaces that are tribologically modified in a way that is beneficial for the tribosystem. In section 4, focus is on the beneficial changes of the outermost surface when boric acid is present. In section 5, surface modifications that take place during initiation of scuffing, a catastrophic type of wear, are in focus. Here, the surface changes are not always beneficial, hence other terms are used for these phenomena.

Classical wear mechanisms that occur in the piston-ring/cylinder contact

The classical wear mechanisms, abrasion, adhesion and tribochemical wear also occur in the piston-ring/cylinder contact, simultaneously or under different circumstances.

If hard particles somehow get into the lubricating oil, abrasion can lead to high wear rates. In other cases, such as in the marine engines in focus of section 5, abrasive so-called cat fines (residue from ceramic catalytic converters used in oil refineries) lead to abrasive wear, which is part of the normal wear even at low wear rates. This could be explained by the rare formation of such scratches and/or that such scratches lead to material being moved around rather than removed from the contact.

Adhesion is part of the wear model described for ultra-low wear rate, although at a small scale and leading to material being moved around rather than removed. Adhesion is also part of scuffing failure, although the scuffing procedure is more complex than only adhesion.

Tribochemical wear or corrosion is also important in some cases. Especially in the marine engine running on heavy fuel oil, which has a high sulphur content leading to high levels of sulphuric acid in the combustion chamber.

3 Research strategy

Friction and wear are characteristics of a specific tribological system. Tribological data are thereby not material properties that should be found in handbooks. In the absence of a fully separating lubricant film, interactions between microscopic surface asperities will determine the friction and wear behaviour. The characteristics of these interactions depend on interplaying system parameters such as load, velocity, temperature and chemical environment. Also the system history, i.e. the parameters that the asperities have been exposed to previously will affect properties of surface asperities and thereby friction and wear.

Consequently, for tribological testing to be meaningful, it should be performed carefully and with tribological knowhow. The key is to simulate the friction and wear mechanisms of a relevant application. This can be more or less difficult, but if not accomplished, the result has little meaning and does not necessarily give any information about the performance in a real application. For instance, if exposing the tribosystem for too high stress in order to accelerate a test, the wear mechanisms might be completely different. If the wear rate is too high, beneficial tribolayers, as those described by Scherge et al. [33] cannot be formed and thereby faulty interpretations can be made.

3.1 Tribological testing and surface investigations

Tribological tests can be performed in numerous ways. Here, the experimental methods used in this thesis are motivated (details are found within the research papers).

Different types of tests, and classification of them as well as important aspects of tribological testing are well described by Axén et al. [44]. Their schematic of a classification of tribotests is shown in *Figure 11*. Naturally, a higher level of test realism is more feasible the smaller the engine/vehicle is. A test fleet of newly developed passenger cars is reasonable, while it is almost impossible to build a single test engine for a large cargo ship.

In this thesis, simplified component tests were developed to simulate some of the properties of real sliding contacts. Such tests are not only faster and cheaper than tests with higher levels of realism. They also offer the possibility of high control of affecting parameters and enable easier interpretation of results by correlation to friction data. Thereby, increased understanding for tribological mechanisms are enabled. The downside is that all parameters cannot be simulated. For instance, velocities used in the tests are only representative for areas close to the turning points of the stroke; the dynamic pressure and temperature resulting from combustion is not simulated; the chemical environment resulting from combustion is not present and the distribution and exchange of lubricating oil is not the same as in the engine.

In the tests performed with boric acid, a base oil was used as lubricant in order to avoid the complexity of using a fully formulated lubricant, whereas the cylinder oil used in the tests aimed to simulate the marine engines was performed with a typical cylinder oil.

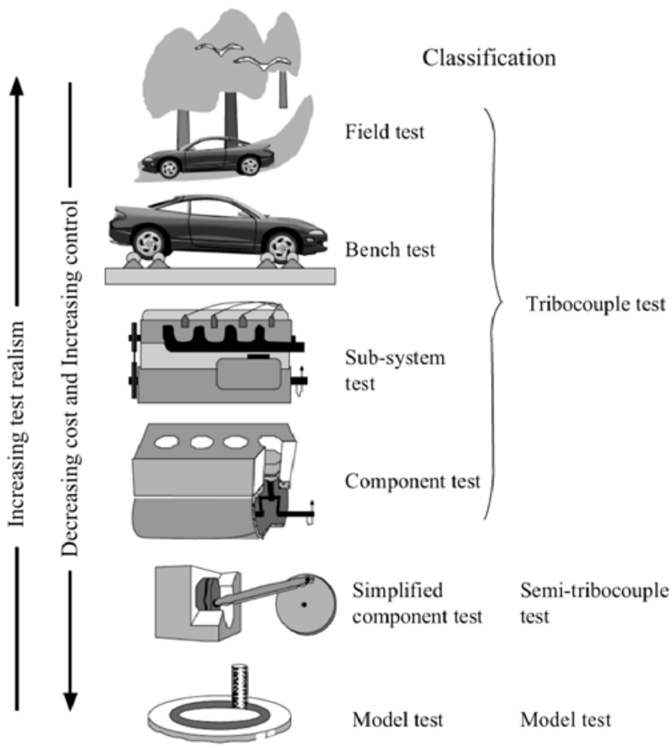


Figure 11. Classification of tribotests according to the degree of realism [44]. Reproduced with permission.

To make sure that test parameters such as surface pressure and temperature are relevant, communication with engineers and scientists within the field has been helpful. However, to ensure that the test is relevant the friction and wear mechanisms must be reproduced in the test. Ideally, this is done by comparing surface characteristics from lab tests with those from the real application. In this thesis, piston rings and cylinder liners both from engines operated with boric acid fuel additive and from well functioning marine two-stroke diesel engines were investigated. However, when it comes to the wear type scuffing, relevant samples are difficult to attain since scuffing happens rarely.

Surface characteristics were obtained by the use of scanning electron microscopy and various types of spectroscopy. In addition to evaluating the relevance of the tests, these techniques have also been used to gain increased understanding of tribological mechanisms. The techniques that have been used are scanning electron microscopy (SEM), electron dispersive X-ray spectroscopy (EDS), focused ion beam (FIB), vertical scanning interferemometry, light optical microscopy, X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy.

Standard tests have not been used in this thesis although they are sometimes used within the tribological society. Such tests are useful for general characterisation of materials with the aim of comparing with previous presented results. However, standard tests are often too far from applications and must not be adopted. In this thesis, reference materials and reference tests are used as an alternative to using standard tests.

3.1.1 Modelling as a complement to tribological testing

Although computer modelling is not a part of this thesis, it should be mentioned that this could be used to simulate the piston-ring/cylinder contact. Different kinds of numerical modelling are used because they can be faster and cheaper than experimental testing. In the modelling, it is possible to include complex effects such as temperature gradients and thermal expansion, which are not easily represented in experimental tests that are often even more simplified than the commonly used sub-system tests. However, the accuracy of computer models are sometimes questioned, and they are generally not better than engine testing since the models are often calibrated with data from some type of engine test [45]. Hence, errors that occur in the measurements will be transferred to the model.

Computer models have become more and more realistic through the years, but no single simulation model can take all effects into account. Simplifying assumptions are required to enable fast enough computing. Therefore simulations are performed with a specific question in mind and only relevant parameters and effects are included in the model, while other effects are simplified or neglected. Factors that are known to have an effect, but that are often neglected, include piston tilt [46], circumferential curvature [13] and oil availability [47].

4 Boric acid for higher energy efficiency in engines

Frictional losses contribute to a large part of the energy losses in society in general as well as in transports. In various components of the engine, friction transforms kinetic energy of the piston into heat, i.e. useful energy is transformed into energy that needs to be cooled away to protect the engine from becoming overheated.

Recent estimates give that 100 million terajoule, that is about one fifth of all energy produced annually, is used to overcome friction [48]. In transportation, frictional losses in the engine stand for about 11% of the total energy use, and in total 25-30% are lost due to friction [4, 49]. Targeting these losses is therefore important to reduce the carbon emissions per travelled kilometre or transported freight.

The use of boric acid as a fuel additive is here shown as one possible solution for immediate increase of the energy efficiency of engines. A background on boric acid as a lubricating additive is given, followed by a summary of the results from **Paper I and II**, but first a background on tribological approaches aimed at reducing energy losses in combustion engines in general.

4.1 Tribological means to increase energy efficiency

In a recent review paper by Wong and Tung, existing approaches to reduce friction in the engine were divided into three categories [11]:

- Design of micro-geometries, configurations and component properties
- Surface engineering, such as coatings and texturing
- Lubricant and additive technologies

Examples from these categories are shortly explained in the following sections. For a complete review, see the paper by Wong and Tung or other sources [4, 45, 50, 51].

4.1.1 Design changes

A design change for reduction of frictional losses could be to reduce the piston ring tension [45]. Thereby the load on the sliding contact is reduced and consequently also the friction force. This could enable HD lubrication during a larger part of the stroke [10]. However, a high enough ring tension is required to avoid the risk of blow-by of combustion gases, which could both worsen the combustion efficiency in itself and lead to high oil consumption and oil starvation in the contact followed by increased friction and wear problems. Optimisation is the key.

Another example of design improvement for increased energy efficiency is to use strategic thermal management of the cylinder to control the engine oil film temperature (increased or decreased cooling of the liner) [11].

4.1.2 Surface engineering

There are numerous available surface coatings, applied with techniques such as physical vapour deposition (PVD), chemical vapour deposition (CVD), electroplating and thermal spraying (Erdemir-review). Coatings are used on piston rings to obtain higher wear resistance and/or lower frictional losses. In combustion engines, the use of DLC coatings has exploded during recent years, but implementations of more advanced coatings are slow [50]. Furthermore, many low-friction coatings, such as MoS_2, only work under specific conditions that are not typical in engines.

Another approach is to use textured sliding surfaces. While plateau honing of the cylinder bore is common practice, laser texturing of both piston rings and cylinder liner is a subject that has been investigated vastly, especially numerically (see review paper by Gropper [15]). The idea is to create dimples that improve HD lift and also act as oil reservoirs at starved lubrication [15, 51].

In general, coatings and textured surfaces are thought to have an effect only in BL and ML. There are, however, theories describing effects of coatings on both the EHD and HD regime [50]. For instance, thermal properties of the coating affecting friction in EHD [52] and that if the coating is non-wetting to the lubricant, it may reduce some of the shear in the lubricant due to wall-slip [53]. The use of lubricating and wear resistant coatings can also indirectly lead to reduced frictional losses in the HD lubrication regime by enabling use of lower viscosity oils due to better protection against high friction and wear in the BL regime. It is not fully understood how much each lubrication regime contributes to the overall energy losses, but it will depend on how the engine is operated [10, 54].

4.1.3 Lubricant and additive technologies

In the 1950s, reducing the viscosity of engine oil could lead to fuel economy improvements of 2-3% [29]. Such easy approaches are more difficult in todays highly refined engine systems, but lubrication companies have many means of improving the oils. Generally, several approaches are used simultaneously. Typically 10-15 additives are present in an engine oil [11].

Types of additives

Viscosity index improvers, friction modifiers, anti-wear additives and extreme pressure (EP) additives are types of additives that affect the friction performance directly. Other types of additives include anti-oxidants, detergents, dispersants and corrosion-inhibitors. These are well described in the review-paper by Minami [55].

Viscosity index improvers work by changing the temperature dependence of the viscosity and thereby they influence the oil film thickness. Friction modifiers, anti-wear additives and extreme pressure additives influence the friction and wear behaviour in BL and ML. Examples of friction modifiers are fatty acids that are chemisorbed to sliding surfaces and hinder asperity contact, and organic salts of molybdate that reacts chemically to form solid tribofilms. An example of anti-wear additive is inorganic phosphates such as zinc dialkyldithiophospates (ZDDPs). Extreme pressure additives, such as dialkyl disulphide are thought to provide controlled wear at high loads and temperatures and can thereby prevent serious failures such as scuffing.

The effects (i.e. friction modification, anti-wear and protection at extreme pressure) of these additives can overlap each other, for instance some compounds provide both friction modification and wear reduction [55].

Research within lubrication technology

Ionic liquids and nano-particles are hot topics in current research in the field of lubricant technology [50]. There is also much development to find replacement and complements to traditional well functioning additives such as ZDDP and MoDTC, which lead to emission of ash and poisoning of after-treatment catalysts. Boric acid is one out of many possible replacements.

Research about lubrication additives is, due to market requirements, not always published. Further, the complex nature of tribochemistry is still under investigation and not fully understood. Tribochemical reactions are special because mechanical energy is transformed into chemical energy [55]. Chemical bonds have to be broken and formed and there are six possible driving forces behind tribochemical reactions. Apart from frictional heat, the most obvious driving force, reactions are also explained by catalytic action of nascent metal surfaces, formation of free radicals by exo-electrons emitted during sliding, elevated pressures, orientation of molecules and shearing of molecular bonds. For further information on tribochemistry, different types of additives and their synergistic effects, see review paper by Minami [55].

Fuel saving potential of lubricating additives

Friction reductions that result from new additives in lubricants and fuels can lead to immediate massive fuel savings since fast implementation to the existing transportation fleet is possible. This should be compared with fuel savings resulting from design changes or surface engineering where implementation is possible only in new engines entering the market or possibly by rebuilding old engines.

4.1.4 Other means to increase energy efficiency

Friction losses do not only take place in the engine of the car, but also in transmissions and tires, approximately 5% respectively 11% of the total energy use in a passenger car [4]. An example of a simple measure for reduced rolling resistance is to implement pressure sensors in the tires to give feedback about the pressure to the driver and thereby enable more frequent adjustments and improved fuel efficiency.

Reduction of frictional losses is not the only possibility for increased energy efficiency. In the paper by Wong et al., other recent and emerging technologies for reduction of greenhouse gases are also presented [11]. Improvements for reduced energy consumption in gasoline engines include the use of smaller vehicles and also reduced mass by use of lightweight materials. Furthermore, improved turbo chargers and improved combustion technology by replacing carburettors with fuel injection systems have lead to increased efficiencies. Diesel engines are generally more efficient compared with gasoline engines, but have more problems with emission of harmful substances. In these, improvements involve high-pressure injection, lower compression ratios by using advanced valve timing, the use of lean burning and advanced after-treatment technologies.

Further means to increase energy efficiency and/or emissions of greenhouse gases include improvements in logistics and the use of renewable energy sources. Renewable energy in the form of biofuels or biogas can be used directly as a fuel, whereas energy from hydro-, wind or wave-power can be used to produce fuels such as hydrogen [56] and synthetic fuels [57], or electricity for electrical vehicles. The development of electrical vehicles has recently taken large steps, but manufacturers continue to develop a variety of alternative fuel vehicles [58]. It is often said that there will have to be many different solutions if fossil fuels are to be replaced by renewable fuel [59]. However, the positive outcome from using for instance biofuels is not straightforward as it also depends on the related land-use-change [60].

4.2 Boric acid as low friction material

Boric acid, $B(OH)_3$, is a crystalline material that is abundant in nature and thereby cheap. It has a layered structure, with a strong combination of covalent and hydrogen bonds within layers, but weak van der Waal forces between layers (see *Figure 12*). This gives an easily sheared material that can work as a solid lubricant, which was shown in the 1990's by Erdemir [61]. In contrast to solid lubricants such as MoS_2 and WS_2 that only work well in dry conditions [62, 63], boric acid works well in humid conditions [64].

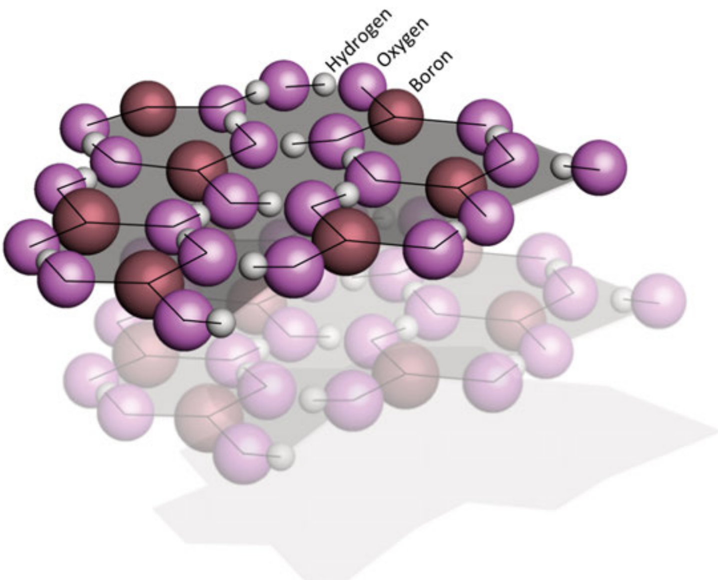


Figure 12. Boric acid has a layered structure. Each layer consists of planar boric acid molecules held together by strong hydrogen bonds. Weak van der Waals forces act between adjacent layers, which means that the material is easily sheared.

Boric acid has been used in numerous consumer products as well as in industrial applications and is considered as relatively safe and benign. Examples of usage are as detergents, fertilizers, in insulation and in metal working fluids. Some health concerns have been raised due to observed developmental and reproductive toxicity effects on laboratory rats exposed to high levels of boric acid [65]. Conversely, no such toxic effects have been observed in studies on highly exposed human populations, e.g. workers in mines. The highly exposed humans had lower concentration of boron in blood and semen compared to control rats that where not exposed to boric acid [65].

4.2.1 Concept of low friction surfaces

A thin layer of an easily sheared material on a harder substrate such as a deformation hardened engine component means that both shear strength and real area of contact between two surfaces is minimized. Thereby, also the friction between such surfaces is minimized. This concept was first observed in 1943 by Bowden and Tabor, who studied the lubricating effect of thin films of soft metals [66]. If it can be assumed that friction is mainly due to shearing between asperities, the friction force is the product of the lowest critical shear stress and the real area of contact:

$$\textit{Friction force} = \textit{Shear stress x Real contact area} \qquad \text{Eq. 2}$$

The thinner the easy-shear layer is, the lower the friction, as long as the asperities do not go through the thin layer. If instead the layer is thick, a high degree of plastic deformation leads to large real contact areas. Consequently, the friction force will be high.

This theory is considered to be valid in dry sliding as long as the real contact area is much smaller than the apparent contact area. In BL, additional effects from shearing of the lubricant and surface-active molecules will take place, but the same concept applies. The combined use of solid and liquid lubricants can also have synergistic effects [51].

Substances in the lubricant can affect the properties of the surface layers because of mechanical mixing and tribochemical reactions.

4.2.2 Boric acid as additive in lubricants

Addition of boric acid particles in oil has been shown to be successful in several studies both targeting engine oils and lubricants for metal forming [67-71]. Commercial products of this kind are available. However, dispersions of particles are associated with agglomeration, which can make such products unsuccessful as engine oils. Kim et al. studied the use of surfactants to keep the dispersion stable over a longer period of time. Friction was reduced when the additive was used [68], but no experiments were performed to evaluate the long-time stability of the dispersion.

Boric acid has also been shown to have potential in applications that are not lubricated by oil. Sawyer et al. showed that boric acid works as a solid lubricant when continuously delivered to the contact in powder form [72]. Rao et al. showed that the lubricating effect in metal forming is comparable to that of grease and graphite lubrication [71]. For more complete reviews of boron compounds in tribology, including organoborates in oils, see Shah et al. [73] and Spikes [74].

4.3 Boric acid as fuel additive – contributions

Paper I and II, focus on the use of boric acid as a fuel additive, rather than the more common use as an additive to lubricating oils. The Swedish company Triboron International AB produces the product that has been used in the tests. The product is mixed into the fuel at a ratio of 1:1000.

To the best of my knowledge, no similar studies have been published. Friction reducing additives in fuels are in general not as common as in lubricants, but several patents that describe the use of boric acid or boron oxide as fuel additive exist.

4.3.1 Field and bench tests with boric acid fuel additive

The commercial fuel additive product in these papers consists of boric acid dissolved in a solvent, mainly consisting of ethanol. In field tests commissioned by the producer of this product, performed by an independent consultancy company, the fuel consumption in cars and stationary diesel generators was reduced with an average of 6 and 10% respectively [75, 76]. Details from these field tests are summarized in **Paper I**. When a large transportation and logistics company used the fuel additive in ten of their light trucks, they observed fuel savings of more than 10% [77]. So-called bench tests, where a passenger car is run under controlled lab conditions and with a specific test cycle, dominated by long high-speed sections have also been performed. This was performed in order to investigate potential harmful effects on after-treatment systems as well as to measure the emission of harmful compounds [78]. It was concluded that the additive did not have any negative effects on after-treatment systems or emissions.

The obtained reductions in fuel consumption are very large compared with the average reduction obtained with other measures to increase the efficiency in these tests. Our research was considered crucial to verify results from field tests and to get a better understanding of the tribological mechanisms behind the large fuel saving effect. An increased knowledge of how different parameters affect performance could also help to optimise the use of boric acid in fuel.

Analysis of sliding surfaces from bench test

It is generally assumed that the low friction obtained with boric acid is due to formation of a tribofilm. The sliding surfaces of piston rings and cylinder liner of one of the engines tested in the bench test were analysed in order to determine if this is the case (unpublished results). With EDS and Raman spectroscopy, no such film could be identified. Using XPS, a peak appeared at the binding energy of the boron peak (B1s). However, interpretation of these spectra is complicated by the fact that phosphor also has a peak close to this energy (P2s) and because of the inherently poor signal to noise ratio for boron. Phosphor is present in the surface layer (confirmed by EDS) since it is part of additive packages in the lubricating oils.

Although no boric acid containing tribofilm could be identified, it is difficult to draw any conclusions from these investigations. There was a period of 13 months between the tests and the first analysis. Thus, if the films are not stable over time, the analysed surfaces might have changed since they were active in the engine.

4.3.2 Evaluation of lab scale test method

In **Paper I,** the aim was to find a simplified lab test that is representative for the application, but simple enough to facilitate an increased understanding of the friction behaviour. Consistently, a setup comprising a reciprocating flat sample (representing the cylinder wall) in sliding contact against a stationary small cylinder (representing the piston ring) and a stroke length of 5 cm has been used. At a load of 5 N, this setup results in an initial Hertzian contact pressure of 60 MPa, and a nominal surface pressure of around 8 MPa as determined by the area of the wear scars after the test. Three approaches of adding the lubricating additive were evaluated; in all cases the surface of the flat sample was also prelubricated with a thin oil film to simulate the engine oil in the piston-ring/cylinder-wall contact. To limit the affecting factors, a synthetic base oil without additives was used (poly-alpha-olefin 8, PAO8). Tests were run both at room temperature and at 100°C, where the latter is supposed to simulate the temperature of the cylinder wall close to the upper turning point. The frequency of motion was 1 Hz and the test duration was 2 000 cycles.

In all tests, the friction was distinctly lower with the fuel additive than for the reference tests, with exception for parts of some tests. The most stable friction results were achieved when a small volume of boric acid solution was repeatedly sprayed onto the prelubricated sliding surfaces. In this type of test, friction reductions of around 20 and 40% were achieved at 100°C and room temperature, respectively. Examples of the friction reduction are shown and compared with references in *Figure 13*. The coefficient of friction is as low as 0.02 during parts of the stroke in *Figure 13a.*

The test procedure was further improved to enable longer and more stable tests and thereby enable the minimal coefficient of friction to spread over a larger part of the stroke (see our poster that is available online [79]). This was done by also adding base oil into the sprayed fuel additive fluid to mimic the replenishment of oil in the engine. With this setup, tests with a duration of 30 000 cycles were enabled (compared to 2000 in **Paper I**). The dual lubrication with fuel additive and engine oil is illustrated in *Figure 14*.

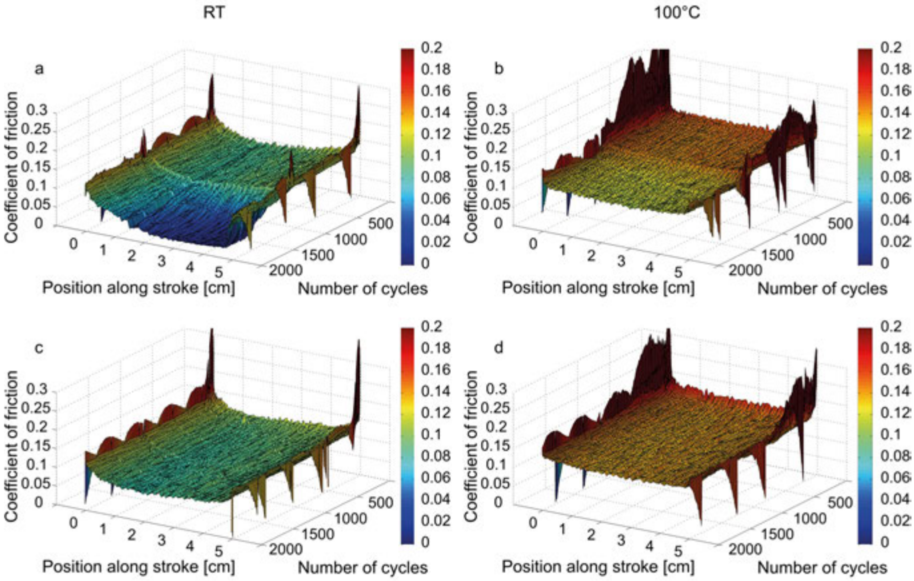


Figure 13. Coefficient of friction curves for individual strokes during the short tests (Paper I) a) Spraying of fuel additive after cycle 1000 at room temperature, b) Spraying of fuel additive after cycle 1000 at 100°C, c) Reference test with predeposited oil at room temperature, d) Reference test with predeposited oil at 100°C. With spraying of fuel additive, the friction drop is larger at one side of the stroke because the spray nozzle is positioned closer to that side.

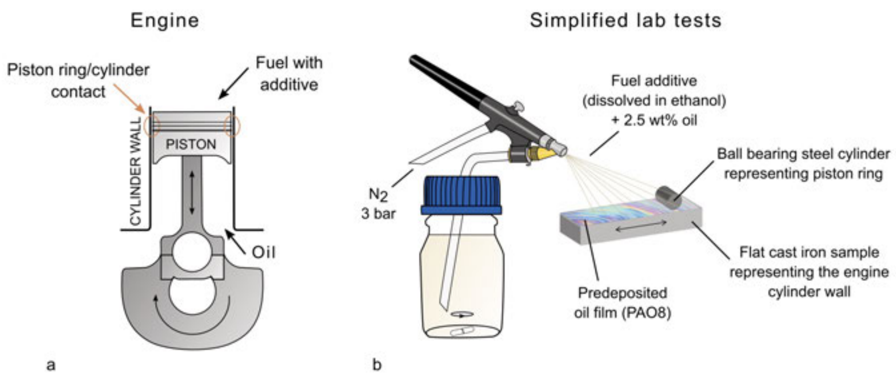


Figure 14. Illustration of the use of the fuel additive in an engine and in the simplified lab tests. a) The piston rings/cylinder contact in an engine with a dual lubrication situation where engine oil is coming from the crankcase and fuel additive from the combustion chamber. b) The piston-ring/cylinder-wall contact mimicked in a reciprocating lab test. The fuel additive fluid is added by spraying with an airbrush onto prelubricated surfaces. The fluid is mixed with 2.5 wt% base oil (poly-alpha-olefin 8, PAO8) to simulate the replenishment of lubricating oil in the engine.

4.3.3 Friction characteristics

Results obtained with the improved test with oil added to the fuel additive fluid are presented in **Paper II**, where also the effect of load and velocity is investigated. In this paper, testing was performed only at room temperature and not at the more engine-like 100°C used in **Paper I**. Room temperature was selected because base oils have low oxidation stability in absence of antioxidants and are therefore not suited for long duration high temperature tests. To verify that we are not comparing the fuel additive results with an irrelevant reference, a reference test with a predeposited film of base oil mixed with 10 wt% of a commercial engine oil additive package was performed in addition to two references with base oil.

The friction results for a test with spraying of fuel additive and oil is compared with three references in *Figure 15.* As soon as the repeated spraying of the fuel additive fluid starts, friction rapidly drops. At the end of the test the coefficient of friction was reduced with 65% compared to the reference with lowest friction.

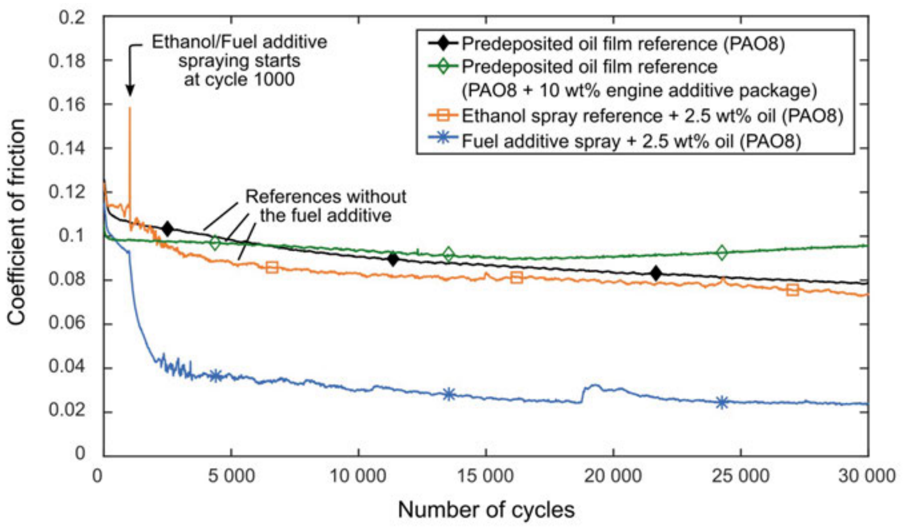


Figure 15. Friction curves (position average over the a full stroke) for four lubrication conditions: the fuel additive spray plus 2.5 wt% oil and three reference baselines without the additive. In all cases, a thin film of oil is predeposited on the flat sample before the test starts (PAO8 if nothing else is stated). In the tests involving spraying, the spraying started at cycle 1000.

The effect velocity was studied after initial running-in tests of 15 000 cycles at 1 Hz and thee different loads. This was done by running short tests (50 cycles) at different frequencies of motion. The results are shown in *Figure 16*.

While the friction curve for the reference is corresponding to the shape of a Stribeck-like curve, the fuel additive curve suggest other lubrication mechanisms. As discussed in the beginning of section 4.2*,* the common explanation for the low-friction properties of boric acid is based on easily sheared lamellae. While this is very likely the case in situations without a liquid lubricant, the results shown in *Figure 16* suggest something else. The difference in shape between the reference curves does not resemble the effect of a solid film with low shear strength, which generally leads to a reduction of the highest friction level followed by a Stribeck-like shape if moving to higher velocities. The friction-velocity curve rather indicates full film behaviour already from the lowest tested speeds. This could possibly be due to formation of a viscous film, as discussed by Spikes [80].

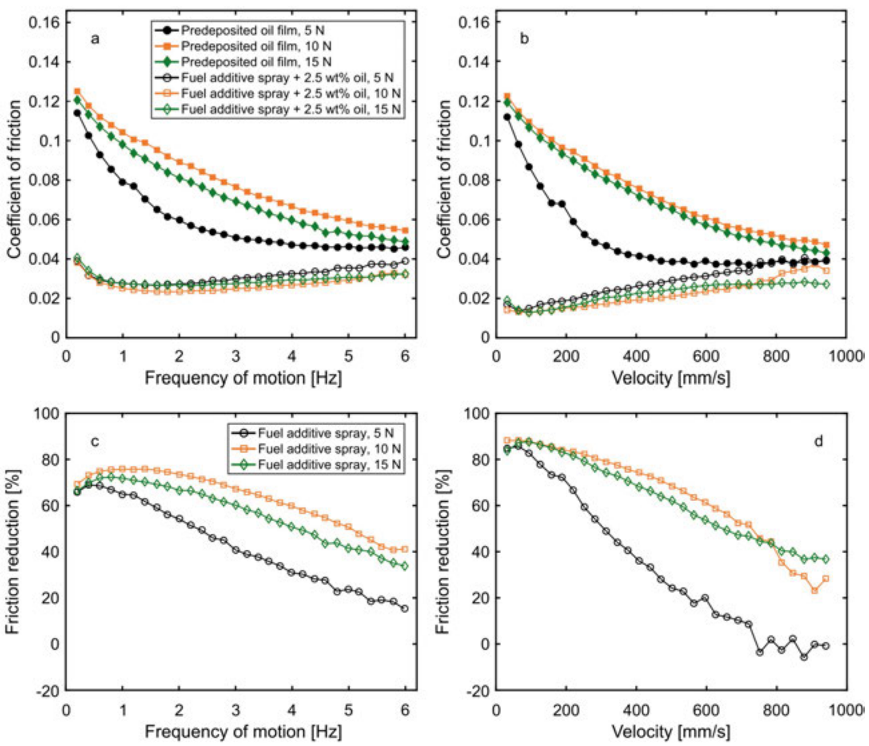


Figure 16. Friction as a function of reciprocating frequency at different loads for the fuel additive and predeposited oil film reference after an initial 15 000 running-in at 1 Hz. a) Coefficient of friction as function of reciprocation frequency. Each point represents the friction average of a full stroke. b) Coefficient of friction versus the average velocity at mid-stroke where the velocity is the highest. Each point represents the average coefficient of friction and average velocity over the central 2-3 cm of the stroke. c) The friction reduction with the fuel additive compared to the reference versus reciprocation frequency. d) The friction reduction with the fuel additive compared to the reference versus velocity over the central 2-3 cm of the stroke.

In the following section (and in **Paper II**), the potential fuel saving resulting from a friction reduction due to the boric acid fuel additive is estimated. Numbers were needed for this estimation and these were taken from the 5 N curves in *Figure 16d,* since the corresponding surface pressure was considered most relevant for those in the engine. The friction data from the two data points at the lowest speed are assumed to represent BL conditions in the reference case, whereas the rest of the data points represent ML conditions.. Based on *Figure 16d,* the fuel additive results in an average friction reduction of 86% compared with the BL reference and 30% compared with the ML reference. These reductions are used in the estimation of potential fuel saving.

4.3.4 Discussion about potential fuel savings

Boric acid can provide large friction reductions in simplified lab tests aimed to simulate its action in engines. This is clear from the results presented in **Paper I and II**. Could this explain the large fuel savings observed in field tests, e.g. 6% in passenger cars [4]. If the friction reduction observed in our lab tests could be translated to the engine, what would the fuel saving be?

To make such estimations, we have to start from the current understanding of frictional energy losses in engines. Literature on the subject is reviewed in the following sections, first with regards to distribution of energy losses between components, and then between lubrication mechanisms. This is followed by estimations of the potential reduction in fuel consumption resulting from the use of boric acid as fuel additive.
between different components.

Distribution of energy losses – components

The piston assembly is generally regarded as the largest source of engine friction [4, 49, 45, 81]. However, the complex nature of a firing engine makes it difficult to measure or estimate both total losses and the breakup A recent effort to summarize and evaluate available information on frictional losses in passenger cars was made by Holmberg et al. to enable their assessment of potential fuel savings due to tribological improvements [4], see *Figure 17*. In their calculations, they assumed that 5.2% of the fuel energy is used to overcome friction in the piston assembly of passenger cars. For comparison, the frictional losses in the whole engine was considered to correspond to 11.5% of the fuel energy, while 5% is lost in the transmission and 11.5% is used to overcome rolling resistance in the tires. The same type of estimation was performed with regards to trucks and buses [49].

A fact that might not be obvious at first is that if the frictional losses are reduced by say about 10% in the engine, which corresponds to a reduction of about 1% of the original fuel energy, this actually leads to a fuel saving of about 3%. This is because when less mechanical power is needed to run the engine, the "useless energy losses", i.e. thermal losses (exhaust and cooling) coming from running the engine, will be reduced to the same degree.

No estimation is better than the data that it builds on. Holmberg et al. state that their assessment is based on the best available published data and conversations with experts in the field. However, the variation in breakdown from different published papers is large [10, 29, 45, 82], and most of the available literature was published decades ago. For instance, the breakdown between thermal losses, in exhausts (33%) and cooling (29%) and mechanical power (38%) originates from a U.S. Department of Energy study that is now over 40 years old. Holmberg et al. state that these numbers are still widely used both by academia and the car industry and that there is no more recent reliable data [4].

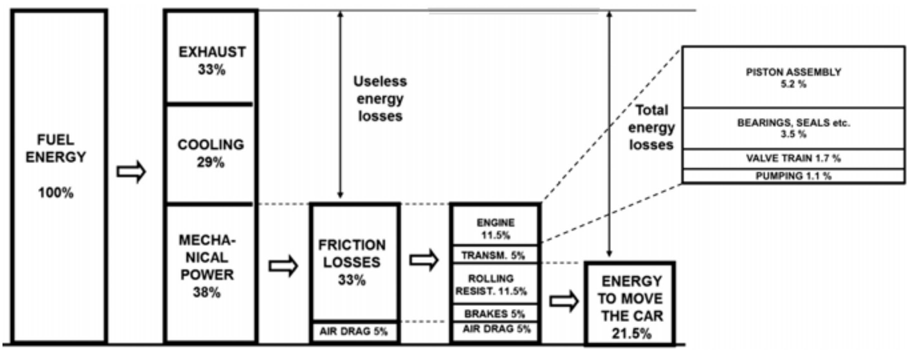


Figure 17. Energy distribution in average passenger cars in the assessment by Holmberg et al. [4]. The engine friction breakdown is added using data from the same publication. Reproduced with permission.

The variation in published figures over the years is partly due to differences between engine/car types as well as differences in driving conditions. For instance, engine friction will constitute a higher percentage of the energy at low loads [83] and idle running. As a consequence, a higher percentage of the energy will be lost to friction during urban driving [10, 11, 54]. There will always be uncertainties in how an estimated energy breakdown from one engine relates to another or to the average engine at average operation. The divergence between available data and the energy breakdown in current engines is possibly large due to the fact that engine development has advanced after most of the energy loss data was published.

The uncertainty of available data also depends on limitations of the studies behind them. Available techniques and methods used for estimations on friction losses are described together with their strengths and weaknesses in the review paper by Richardson [45].

It is clear that there are large uncertainties regarding the available energy breakdown numbers. However, these numbers are the best that we have and will be used in the estimation.

Distribution of energy losses – lubrication mechanisms

The large and rapid variations in load, speed, temperature and lubricant availability make it difficult to estimate the distribution of energy losses between the lubrication mechanisms in the piston assembly. Moreover, the friction and wear mechanisms are not fully understood. It is often stated that HD lubrication occurs during a major part of the stroke, and consequently the major losses are due to viscous forces in the oil film [29, 82, 84, 85]. In line with this, it is sometimes stated that the friction losses coming from BL are small or insignificant and that approaches for reduced BL friction are not important [29]. Taylor and Coy stated that in general, friction modifiers are beneficial in gasoline engines of passenger cars, but not in heavy-duty diesel engines [82].

It is beyond the scope of this thesis to determine which studies are more reliable and more relevant for an average engine of today. However, to somewhat sort it out, I find it relevant to look at this in a historic perspective.

In the review paper by McGeehan 1978, he states that from 1925 and forward, many considered ML to occur to different degrees between piston rings and cylinder liner. McGeehan self stated that there was predominantly HD lubrication with only sporadic local contact around the top dead centre. One reason for this conclusion seems to be the observed low wear rate, as well as the low incidence of scuffing [29]. This should be seen in light of the prevailing understanding of sliding surfaces. More recent theories (see section 2.2.5) can explain the low wear rate even with asperity contact.

There are research results that indicate that HD losses are not always the major friction mechanism in the piston assembly [14, 86, 87].

Further, engines have gone through many changes since much of the research was produced. This includes changes towards minimization of combustion of lubricants [88], reduced viscosity of the engine oil and increased combustion pressures. Hence, the oil availability as well as the possibility to form a full film is not the same today as in earlier engines. Many researchers have reported on the importance of considering oil availability when simulating lubrication, since starved lubrication inhibits the generation of HD pressure in the lubricant [24, 89, 90, 47, 91]. As an example, the results by Rehl indicate that there is a low portion of HD friction at the compression stroke, since the oil is scraped away on the preceding down stroke [14].

Nevertheless, numbers are needed for estimations, but few researchers have presented average numbers. In their calculations, Holmberg et al. presumed that the friction loss for the piston assembly was divided into 40%

from HD lubrication, 40% from EHD lubrication, 10% from ML and 10% from BL [4].

Estimation of potential fuel savings

As discussed, available friction loss data carries large uncertainties and will vary between different car types as well as depend on the driving parameters. There are uncertainties also regarding how well the present friction investigation represents the friction in the engine. Nonetheless, in **Paper II**, we wanted to explore various scenarios for how a large friction reductions could results in large fuel savings. This was performed as an attempt to assess if the fuel efficiency improvements found in field tests can be explained by friction reductions in the piston assembly.

As a start, if assuming that the friction in BL and ML in the piston assembly is reduced as in our lab tests (as described in section 4.3.3), the fuel saving would be 1.6% when using the same friction loss break-down as in the Holmberg study [4]. This is illustrated in in *Figure 18*. With a friction reduction of 86% in the BL regime, the energy losses are reduced from 0.5 to 0.07% of the original fuel energy. Similarly, with an average friction reduction of 30% in ML, the losses are reduced from 0.5 to 0.36%. The friction in the piston assembly is consequently reduced from 5.2 to 4.6% and the energy needed to run the engine is reduced, from 11.5 to 11.0% of the original fuel energy. Energy losses from sources that are regarded as HD and EHD are unaltered as are the energy losses coming from bearings, seals, valve train and pumping. With unaltered values also for friction losses in tire road contact, transmission and brakes, the total friction loss is now 32.4% compared with 33% in the original estimation. The same energy is needed to move the car, but less energy is now needed to run the engine. This means that the other energy losses originating from running the engine, i.e. thermal losses in exhaust, as well as heat that is cooled away, will be reduced at the same degree as the mechanical energy, i.e. from 33 to 32.5% and from 29 to 28.5% respectively. Under said assumptions, the resulting fuel saving would be 1.6%.

A fuel saving of 1.6% can be considered as a significant fuel saving. In the total fleet of passenger cars, it would lead to global fuel savings of 10 100 million litres per year and corresponding reductions of CO_2 emissions, estimated with the data for the year 2009 presented by Holmberg et al. [4]. However, it is a small fuel saving compared with those observed in field tests, where the average fuel saving was 6% [75].

To reach fuel savings close to these 6%, further assumptions are needed, we need to assume that the running conditions of the passenger cars in this study result in friction loss breakdowns different from that in Holmberg et al.

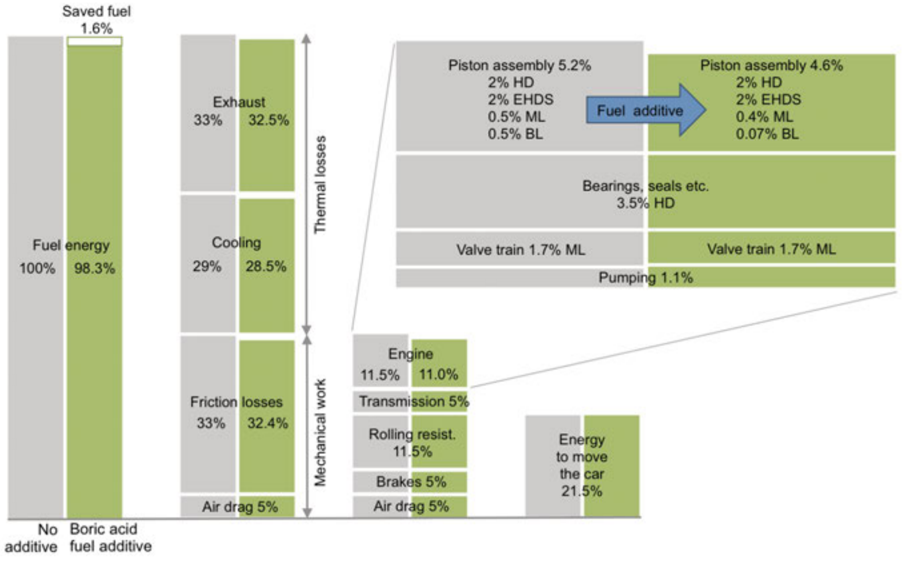


Figure 18. Illustration of estimated energy loss reductions. Grey bars represent the energy break down used by Holmberg et al. [4] and green bars represent the modification of energy distribution due to the assumed friction reduction due to boric acid additive. Both reduced numbers and reduced height of the bars illustrate the energy loss reductions resulting from this assumption. EHDS - EHD in sliding contacts.

There are a number of factors that give rise to uncertainties in the estimations for energy loss breakdown that could lead to both under- and overestimations of the fuel saving. In **Paper II** we have explored the effect on the fuel saving that would come from various changes in energy breakdown. In our exploration, we assume that in a passenger car at a specific operation, the friction losses from BL and ML in the piston assembly can be twice those assumed by Holmberg et al. We further assume that the piston assembly can be a larger and the bearings a smaller source of the total losses and that the air drag can lead to lower losses. Instead the losses from cooling and friction are larger. With these assumption, and assuming the friction reduction as in our lab tests, the resulting fuel saving would be 4.1%.

In addition, boric acid may also have an effect in the valve train, which is considered to be operated in ML [4]. This is not something that has been investigated, but it is not unlikely that boric acid could end up in these contacts. It is well known that soot particles from the combustion end up in the valve train and cause wear [92]. A friction reduction of 30% in the valve train would lead to almost a doubling of the reduction in fuel consumption.

Presented combinations of assumptions could lead to the fuel savings observed in field tests. In other words, it is not unlikely that a considerable friction reduction in the piston/cylinder contact could lead to fuel consumption reductions around the observed 6%.

With an alternative approach, we can avoid the quite uncertain breakdown between different lubrication mechanisms. If just assuming that the effect of the fuel additive is mainly due to the piston-ring/liner contact, how would the friction during the strokes have to be modified to give a fuel saving of 6%? If using the same energy breakdown as in Holmberg et al. the energy loss in the piston assembly would have to be reduced from 5.2 to 2.9% of the original fuel energy. This corresponds to a total friction loss reduction of 44%. If taking a friction curve from a floating liner test of a fired engine as an example (same data as presented in *Figure 6*, from Rehl [14]), a curve that would lead to a reduction of 44% could for instance look like the green curve in *Figure 19*.

Possibly, also mechanisms unrelated to friction could result in fuel savings. One such idea is that the additive enhances the combustion, related to the effect of boron nanoparticles presented in [93].

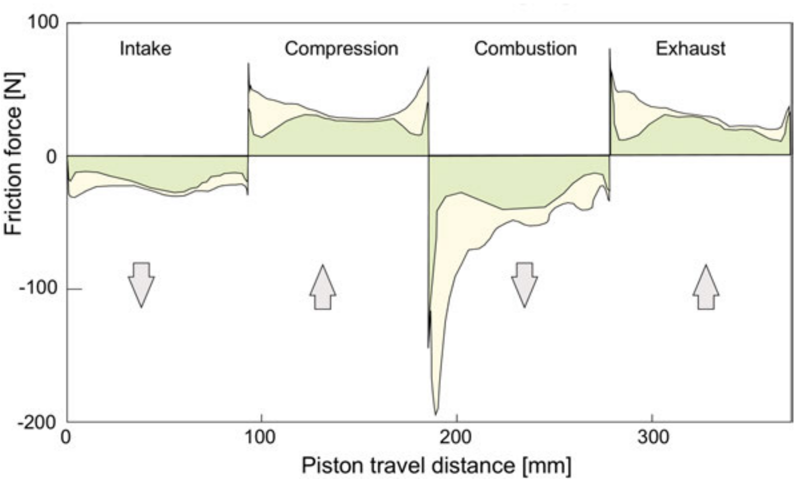


Figure 19. Illustration of how a reduced friction corresponding to a 44% frictional energy loss reduction in the piston assembly could be distributed over the four-stroke cycle. According to the energy loss breakdown by Holmberg et al. [4], this is the reduction required to reach the 6% fuel saving observed in field tests. The reference friction data curve is from [14], same data as in Figure 6. To comply with the friction character achieved in the fuel additive tests, the friction reduction in this sketch is most significant at the turning points and in the nearby low speed regions.

4.3.5 Tribofilm formation

In **Paper I**, surface analysis of the wear scars after the tests revealed tribofilms containing boron and oxygen. This was determined by EDS, see *Figure 20* where an SEM image and EDS mappings of the flat surface from a test at 100°C is shown. The chemical bonding of elements in the tribofilm was investigated with XPS. The results indicate that both boric acid and boron oxide (B_2O_3) is present. The presence of boric acid in tribofilms formed in room temperature tests was further confirmed with Raman spectroscopy (unpublished results).

The characteristic of the tribofilm depends on test temperature. The film of boric acid on the flat sample covered a large part of the sliding surface in the room temperature test, while it was primarily seen on the sliding plateaus in the 100°C (see *Figure 21 and 20*). The larger amount in tests at room temperature was because at 100°C, part of the fluid evaporated before reaching the surfaces.

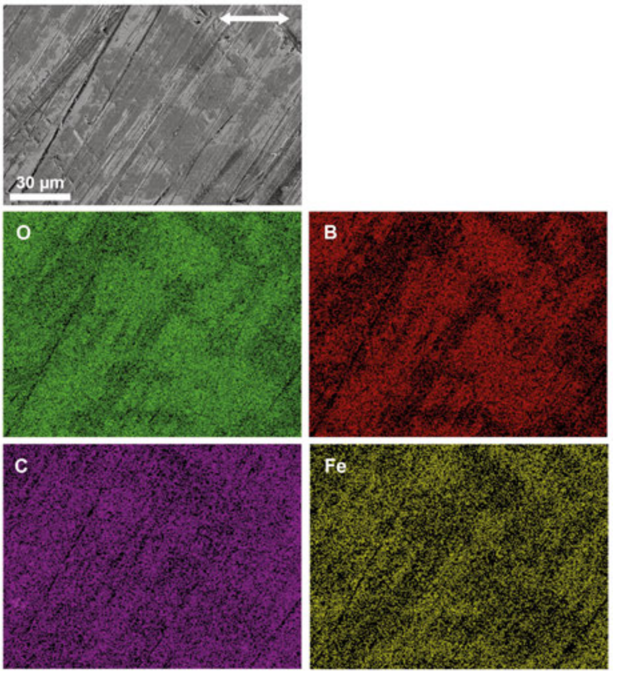


Figure 20. Flat sample surface from sort tests with spraying of fuel additive fluid on prelubricated surfaces at 100°C. SEM image with corresponding elemental EDS mappings of oxygen, boron, carbon and iron. Oxygen and boron is found on sliding plateaus.

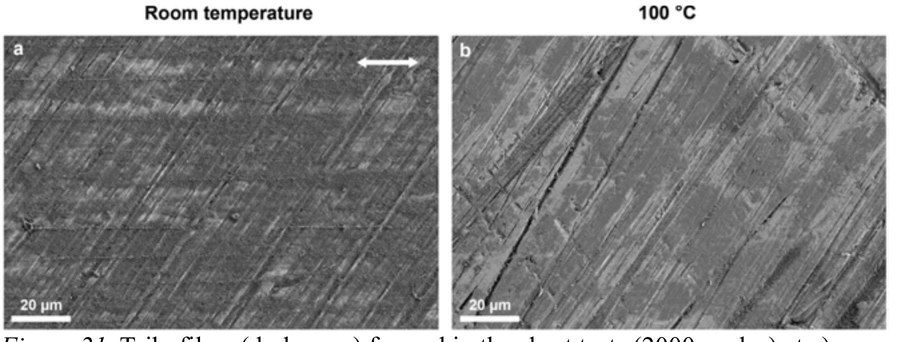


Figure 21. Tribofilms (dark-grey) formed in the short tests (2000 cycles) at a) room temperature and b) 100°C. SEM.

Difficulties with analysis of tribofilms

The formed tribofilms were not stable over time. The difference between analysing samples immediately after the test, or several days later was substantial (see *Figure 22*). Similar findings were made by Gaillardet et al. regarding boric acid sublimation in organic solutions and dried residues thereof [94]. This insight might explain problems of finding these types of tribofilms on samples from field-tested engines. Thus, this finding is vital for future research. In *Figure 22*, it is also clear that the carbon signal is higher in the latter test. This is probably because carbon contaminants have migrated to the analysed area during the first analysis and formed a thin layer on top of the tribofilm. Absorption of X-rays in this carbon-layer could explain the decreased boron signal even without sublimation of boric. However, the increased signal for iron in the latter test suggests that some of the boric acid actually has disappeared.

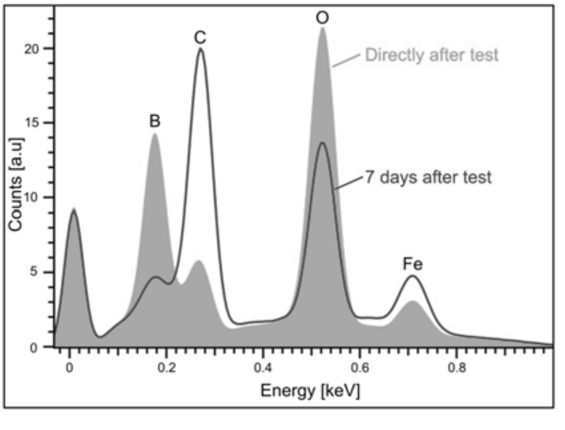


Figure 22. Example of EDS spectra of the boron and oxygen containing film on one of the plateaus in *Figure 20* One spectrum acquired directly after test and one seven days later.

5 Scuffing – a tribological problem expected to increase

5.1 Need for reduced sulphuric emissions

The catastrophic wear problem called scuffing is expected to increase when the fuel in large cargo ships is changed to reduce sulphuric emissions. Scuffing is a reliability problem since it happens unexpectedly and when it happens, the cylinder liner has to be replaced, which is costly and time consuming. Preventing scuffing also has a safety aspect; when at sea, engine power must be fail-safe. These aspects are all important in the shipping industry.

Large cargo ships are currently operated on sulphur-rich heavy fuel oil (HFO). This fuel is the remaining fraction left at the bottom of the refinery when other fractions, such as petrol, jet fuel and diesel have been distilled from crude oil (see *Figure 23*). HFO is black and solid at room temperature and the same type of product is used in asphalt. It is used as fuel because of its low price. The downside is its high concentration of sulphur, and consequently large emissions sulphuric compounds (SO_x), as well as occasional corrosion problems due to formation of sulphuric acid [95].

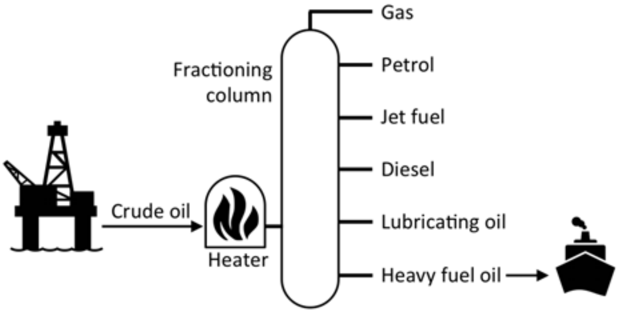


Figure 23. The cheap, sulphur rich heavy fuel oil is the remaining fraction when other types of fuels and oils have been distilled from crude oil. It is commonly used in cargo ships.

Historically, emission legislations have not been as tough for marine transports as for land transports. This is partly due to the relatively low emission level per transported freight. According to the *International Energy Agency*, shipping is the most sustainable way of transporting freight [96]. Another factor behind the difference in legislation is the difference in severity of certain pollutants on sea and land. Harmful emissions of SO_x and NO_x are mainly a problem for human health, [97] and ecosystems on land and in lakes, as well as for sensitive building facades and cultural heritage. Because of this, legislations for marine transports are generally harsher in coastal regions.

However, maritime transport is a significant and increasing source of air pollutants [98]. Nearly 70% of ship emissions occur within 400 km of coastlines and emissions can be transported large distances in the atmosphere from sea to land [99]. Upcoming regulations are more rigid, both SO_x and NO_x emissions have to be reduced [100].

5.1.1 Fuel without sulphur for reduced emissions

Reducing sulphuric compounds from the exhausts can be done by removing sulphur from the fuel or by removing it from the exhausts with after-treatment, such as scrubbing. The previous option is related to the tribological problems investigated here.

This research has been part of a project aiming at developing a new type of two-stroke diesel engine that can run on compressed or liquefied *natural gas*, which contains no sulphur. This almost eliminates emissions of SO_x (some HFO is still used as pilot fuel in this type of engine), and this change is also expected to lead to reduction of NO_x by 24% [101]. Another positive effect of changing to natural gas is reduced emissions of greenhouse gases. Juliussen stated that the emissions of CO_2 could be reduced by approximately 20% [101], but in other assessments, these numbers are lower [102, 103].

5.1.2 Wear problems associated with low-sulphur fuel

According to ship owners, ships operated on diesel with low sulphur content have a higher risk of the catastrophic type of wear called scuffing (scuffing is further explained in section 5.3). Experimental studies have also shown that fuels with lower sulphur level offer worse scuffing resistance [104, 105].

The concern of higher scuffing risk was the motivation for **Paper III, IV and V**. In **paper III,** the aim was to understand the effect of sulphur on the tribological performance in a well functioning engine. In **paper IV and V,** the aim was to investigate the possibility to test scuffing resistance of piston ring materials and to understand the scuffing phenomenon better.

It is not unusual that changes aimed at reducing environmental problems cause problems in tribosystems of the engine. A classic example of this is when the anti-knock additive tetraethyl-lead was removed from gasoline (starting in the 1970s). Increased wear of exhaust valves occurred due to the lack of the previously formed tribofilm of lead compounds protecting the surfaces [106]. More recently, the risk of high wear of exhaust valves is again an important topic. This time connected to regulations on emission of harmful particulate matter. As with the lead compounds, the particulate matter has been shown to form a protecting tribofilm on the valves [107, 108].

5.2 Effects of sulphur in well-functioning engines

The lower risk of scuffing with higher sulphur content in the fuel is often ascribed to build-up of a solid lubricating film and sometimes to a mild beneficial corrosive wear. The former is supported by research performed on various sulphur containing EP-additives [109-112], including elementary sulphur, organic disulphides and ZDDP, which react with the surface to form tribofilms. The idea that a mild corrosive wear could be beneficial is realistic if it keeps the graphite structure open. An open graphite structure as well as small pits in the surface caused by corrosion could work as oil reservoirs, as is the case of surface texture [113]. The benefit of a mild corrosive wear could also be related to theories about the necessity of a low, but high enough wear rate to avoid scuffing [114]. Another possible benefit is that the sulphur compounds dissolve oxidised oil deposits, sometimes called liner lacquer, that can form and fill the honing grooves [115].

The aim of **paper III** was to get increased the knowledge about the role of sulphur for the tribological performance during normal running.

5.2.1 Sliding surfaces from field and lab tests - contributions

In **Paper III**, piston rings taken from a marine engine operated on sulphur rich HFO were investigated within a week after removal from the engine. On the sliding plateaus of these worn rings, no sulphur or calcium (both present in cylinder oil) was detected. In contrast, tribofilms containing these elements were detected on both mating surfaces from simplified lab tests. Also the appearance of the sliding surfaces differed between field worn and lab-tested surfaces. In *Figure 24*, the appearance can be compared, and the distribution of sulphur is shown in the EDS-map of the lab-tested surface. Since EDS analysis is not very surface sensitive, sulphur might be present on field worn rings even though it was not detected. The results, however, show that if there are sulphur-containing tribofilms on the field worn rings, these must be much thinner than on the lab-tested surfaces.

After **paper III** was published, a small sample drilled out from a cylinder liner was investigated and sulphur could be detected on the surface (see *Figure* 25). Evidently, sulphur could be part of the tribofilm on the sliding surfaces in the engine, but this is not always the case.

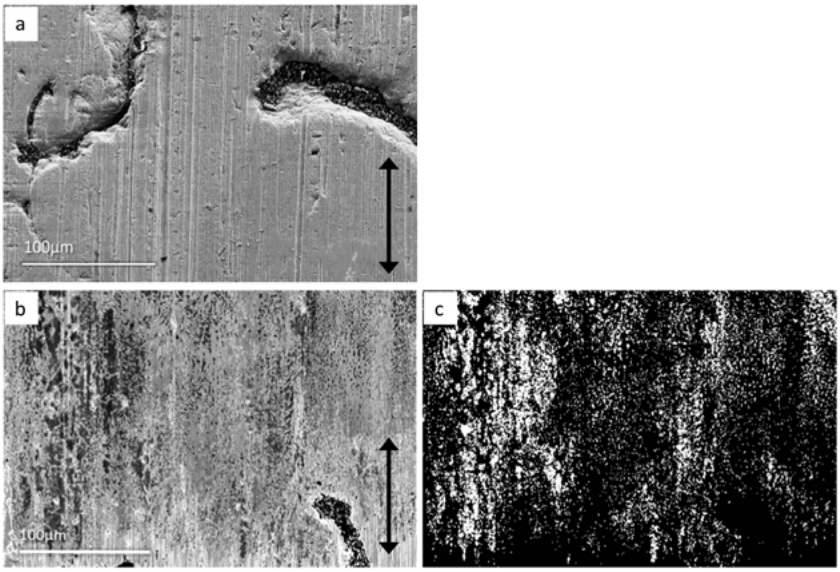


Figure 24. Typical appearance of surface of a) well running piston ring from a marine two-stroke diesel engine, and b) sample in lab test. C) EDS map showing sulphur distribution over the area in b. No such sulphur containing films were detected on piston rings from engine. Sliding direction is vertical in the micrographs. SEM.

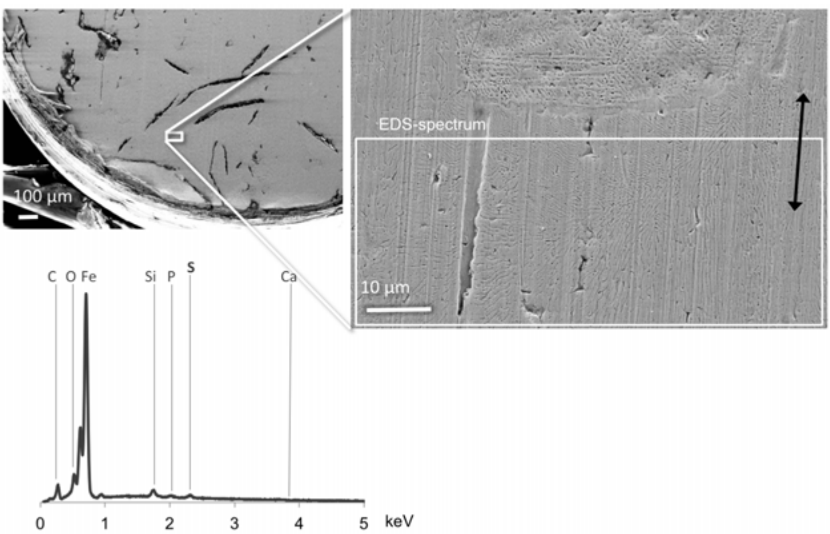


Figure 25. Sample drilled out from the cylinder liner of a marine two-stroke diesel engine. Part of the sample is shown in the upper left corner. The inset shows the area of EDS data collection. EDS spectrum in the lower left corner. In contrast to the examined piston rings taken from another engine, sulphur was detected on the surfaces. SEM.

The difference in appearance (between surfaces from field and lab tests) show that the lab tests were not simulating normal running. Nevertheless, results from these tests could be valuable for an increased understanding of the role of sulphur.

An interesting result was achieved when comparing samples from tests performed either with *fresh cylinder oil* or with *used cylinder oil* (drained from a marine engine). The aim with the latter was to better simulate the conditions in an engine operating on sulphur-rich HFO. The used oil has a higher concentration of sulphur because of sulphur coming from the fuel, (about 2.4% compared with 1.1% in fresh oil where it is present in the additives). Tests with used oil resulted in surfaces with a higher amount of sulphur compared with samples run with fresh oil.

The coefficient of friction was somewhat higher with fresh oil than with used oil, 0.11 compared with 0.10. However, since the oils are different in other aspects than just the sulphur content, it is difficult to draw any conclusions about a friction reducing effect of sulphuric compounds from these results. Ideally, friction should be compared between used oil from ships operated on HFO and low sulphur fuel, to exclude other effects in used cylinder oil.

The results do not exclude that operation on sulphur rich fuel results in a mild beneficial corrosive wear. It is, however, difficult to see that sulphur would play a role for the tribological performance in a well-functioning engine by being part of a lubricating tribofilm. Possibly, sulphur-containing tribofilms are only formed when lubrication is failing and/or local surface pressures are increased, i.e. when a lubricating tribofilm is needed. Perhaps, the performed lab tests resembled running-in (with relatively high degree of plastic deformation of asperities) rather than normal running. Dienwiebel et al. considered a similar explanation when they did not find protective antiwear film during normal stressing of the piston-ring-bore tribosystem [28]. This is also consistent with the function of EP additives that react with tribosurfaces when conditions become severe [55].

The fact that sulphur containing films were formed in comparatively short lab tests shows that sulphur-containing films can be formed; and the higher concentration of sulphur in tribofilms formed with *used oil* suggests that the tribological performance could be affected by sulphur in the fuel.

5.3 Scuffing – vastly investigated, poorly understood

Scuffing is a catastrophic type of wear, involving a sudden transition from a normal low wear rate to a very high one. It is often said to happen infrequently and unpredictably to a few among many well functioning engines, i.e. not after a certain amount of running or a certain amount of wear or at specific known parameters. It is sometimes possible to see causes for why it would happen at a certain point, but far from often.

The definition in the ASTM Terminology standard G40 is:

> Scuffing is a form of wear occurring in inadequately-lubricated tribosystems that is characterized by macroscopically observable changes in texture, with features related to the direction of motion.

This definition clearly pinpoints the result of scuffing, and also that inadequate lubrication is part of scuffing failure, but it is not clear what the initiating mechanisms are or how lubrication becomes inadequate. Although engineers and researchers have investigated the causes and mechanisms of scuffing during 80 years, it is often said that scuffing is poorly understood [116, 117].

5.3.1 Difficulties in studying scuffing mechanisms

One reason behind the insufficient knowledge about scuffing is probably that once it has started, the wear is accelerated and the surfaces quickly become completely destroyed due to increased blow-by. It is therefore difficult to investigate the initiating mechanisms by analysing failed surfaces [118].

Another reason for confusion about the mechanism might be that the term scuffing is used in many different applications, such as piston-rings/cylinder pair, cam/follower and gears. Poor lubrication and the resulting appearance of failed surfaces is the common denominator. However, large differences in contact mechanics and temperatures suggest that there might be different initiating mechanisms. In literature, scuffing is sometimes investigated and discussed in general terms, not always with a specific application in mind. It is better to clarify which application that is targeted when doing research on scuffing.

To further complicate the picture, there are several terms used for similar phenomena, sometimes for the same and sometimes for different distinctive phenomena. These terms are scuffing, scoring, galling and seizing. Scuffing and scoring are both used for metal parts that are normally well lubricated [119]. Sometimes they are used to describe the same phenomenon, but in other cases they are seen as similar, but distinctly different forms of failure [120]. Galling is generally used to describe contacts with low sliding speed and no or sparse lubrication. Seizing is used to describe severe damage where sliding is completely suppressed due to high friction. This could be seen as a later stage of failure. Here scuffing is considered the same as scoring and the same as a pre-stage to seizing, whereas galling is considered a different phenomenon.

5.3.2 Need for better understanding of scuffing

The mechanisms behind scuffing might not be completely understood, but the severity and consequences of scuffing failure bring about high incentives for understanding it better.

The problem of scuffing seems to have been solved for cars and trucks, whereas it still occurs in large marine engines. One reason for why the problem of scuffing is not yet solved for these huge engines is that they are produced in low numbers. Due to their size and cost, it is simply not possible to produce a large test fleet or several test engines to test out new designs and material solutions. New design changes are instead implemented into engines that are sold, and tests are performed on vessels in operation. Hence, these engines are always at the development stage.

Even if scuffing is not as big a topic in the automotive and truck industries, it can still become an issue during development stages [114]. A better understanding of the mechanisms of scuffing could facilitate optimisation of design, sliding materials, lubrication technique and lubricating oil also in these areas.

To gain knowledge about scuffing, studying the mechanisms in situ in the engine would be ideal, but also impossible. Instead, the mechanisms have to be studied in simulating tests. Combined with insights and knowhow from real engines; an increased understanding could be achieved. The aim of **paper IV** was to investigate the potential of enabling material selection from lab tests and the aim of **paper V** was to test new materials. In both papers, the initiating mechanisms of failure in scuffing tests were studied. Results from these tests are summarised in section 5.6 and 5.7 after the following literature review.

5.4 Review of literature on scuffing mechanisms

Throughout the years, much effort has been made to come up with scuffing models and condition criteria with the aim to understand and/or predict scuffing. Although many of them have value, none have proven to be fully satisfactory and no consensus has evolved for preference of any model.

For a historic perspective and to give a brief summary of performed research, examples of published models and theories are presented and discussed here Subheadings are used to organize the different models, but many models could be classified under several of these sub-headings.

More comprehensive reviews and more details are found in review-papers [116, 121] and in the specific references.

5.4.1 Critical temperature

Blok is often mentioned as the first to publish a theory involving the importance of local surface temperature [122] (Blok used the term seizure, and focused on gear contacts). According to this theory, scuffing would occur at a specific local temperature for a specific material/oil combination. This temperature was considered as the result of bulk temperature and a superimposed friction dependent flash-temperature. The latter is a function of the coefficient of friction, load and sliding speed.

The critical scuffing temperature has been validated by some researchers, while others reported on inconsistencies [123, 124]. From reviewing many studies with scuffing tests, Dyson concluded that the critical contact temperature could not be constant except for at very narrow ranges of loads and velocities [125]. Further, a disadvantage with the different thermal models is that the coefficient of friction is needed to estimate the surface temperature. It is inherently difficult to estimate the friction in a contact and the friction changes over time [117, 125].

Blok did not present any explanation for what mechanism that occurs at the critical temperature. However, it is obvious that temperature affects for example the lubricant viscosity and the hardness of materials. Several theories have been proposed regarding possible mechanisms for scuffing at a specific temperature. One hypothesis is that scuffing occurs at a critical temperature due to desorption of polar molecules that otherwise protect the surfaces [126]. Another is that thermal instability leads to mechanical collapse of the lubricating film [125, 127] or to thermal expansion of asperities [128, 129]. There are also theories on lubricant decomposition due to thermal oxidation at high temperatures [130]. Another one is that at a critical temperature, the rate of surface oxide formation becomes lower than the rate of oxide removal [131].

5.4.2 Friction power intensity

The friction power intensity criterion is another scuffing criterion. It was first presented by Matveevsky in 1965, although he called it “specific power of friction” [132, 133]. It is the product of coefficient of friction, contact pressure and sliding speed, which is basically the rate of energy transformation and dissipation per contact area. Hence, this can be seen as a thermal criterion just as Bloks criterion.

In early literature, there were a good correlation between this criterion and experimental results. In Dyson’s review 1975, friction power intensity seemed to have the widest range of application compared with the total contact temperature and the film thickness, which were also shown to be approximately constant in specific ranges of parameters [125]. The difficulty of estimating the coefficient of friction makes also this criterion limiting. Further, it is not possible to calculate the real contact pressure in an application where plastic deformation occurs. The full power of friction, which uses the normal load in the contact instead of the contact pressure is a better option if contact areas change [125, 132, 133]. However, this value is expected to vary with size of the machine.

5.4.3 Breakdown of lubricating film

Dyson presented a model in 1976 where scuffing would occur when asperities come in contact due to collapse of EHD-films [134]. Like many of the previous models, this model includes a thermal criterion, but the surface roughness is also an affecting parameter.

Another common criterion is that of a specific surface finish/roughness given in terms of R_a value or bearing areas. In models describing oil film thickness, it is assumed that scuffing would not occur as long as the film thickness is larger than the surface roughness [116]. The roughness is often considered to be constant in models used to predict failing criteria, but it is evident that the initial roughness will change during running [135] as well as during a progression towards failure.

However, collapse of lubricant film does not always lead to scuffing. A large degree of asperity contact can take place without leading to scuffing [33, 117]. As Bowman and Stachowiak suggests, the lubricant film could rather be seen as a first line of defence and breakdown of this is generally seen as a necessary, but in itself an insufficient condition or scuffing to occur [117].

The next line of defence is perhaps a solid lubricant film. Several researchers have suggested the importance of removal of protecting surface films for scuffing to become initiated [116, 131, 136]. Saedi et al., recently proposed a theory for scuffing initiation that involves formation of protective iron oxide layers during lubricant starvation, followed by gradual reduction of this layer (with carbon as reducing agent) until ferrite (α-Fe) is formed [136]. When pure iron is formed, this would lead to metal-metal contact, adhesion and major transfer of material leading to a self-accelerated aggravation.

5.4.4 Critical stress or plastic deformation

Several criteria, connected to deformation of materials, have been developed. The plasticity index [137] is an examples that was under active discussion in the 1970s and according to this theory, elastic deformation would transform into plastic flow of asperities. This was supported by results by Hirst and Hollander [138], but Park and Ludema showed that the plasticity index is not useful indicator to predict scuffing failure [119]. Also, the fact that plastic flow has been shown to be important even at ultra-low wear [33] makes these criteria less interesting.

Ajayi and Hersberger and co-workers proposed that adiabatic shear instability in the near surface material is the mechanism behind scuffing [139, 140]. As the severity of a contact increases, adiabatic shear instability takes place when the rate of thermal softening locally exceeds the rate of work hardening. Plastic deformation would then take place locally and create an unstable situation. Yagi et al. performed scuffing tests where the results strengthened this hypothesis [141].

5.4.5 Low cycle fatigue

A hypothesis presented by Kim and Ludema [142] is that the surface fails before the lubricant fails. This would occur through accumulation of plastic deformation, so-called low cycle fatigue, in the subsurface leading to formation of wear debris. Debris particles agglomerate to form larger particles that are work-hardened in the contact. When a large particle carries most of the load, the contact stress will be so large that the fluid lubricant fails. The temperatures consequently increase, protective films are altered and adhesion starts to occur. They found good correlation between low cycle fatigue and scuffing tendency for a range of steels with different hardness. This theory introduced time/history dependence into the mechanisms behind scuffing failure.

5.4.6 White layer formation

Scuffing has been described as formation and spalling of a so-called white layer [143]. This is a hard and etch resistant layer that is called white layer because of its white appearance in the light optical microscope after etching. Such white layers are formed on components in several applications and can have different composition [144]. Rogers described it as a specific phase [143], but many descriptions are found in literature [118], including fine-grained structure and a fine dislocation network.

5.4.7 Accumulation of wear debris

Enthoven and Spikes proposed that accumulated wear debris could initiate scuffing by preventing oil from coming into the contact [145]. This in line with results presented by Holzhauer and Ling [146], who observed that wear particles adsorbed oil and/or stopped oil from coming into the contact. Li and Yagi and co-workers similarly observed that entrapment of agglomerated wear debris in the contact was initiating scuffing [147, 148]. Possibly, accumulated wear debris could disturb the pressure distribution and thus cause high local pressures and heat generation. The mechanisms presented by Kim and Ludema, described earlier, includes a similar mechanism [142].

5.4.8 Time/history dependent mechanisms

Several of the described scuffing mechanisms, including low cycle fatigue, white layer formation and accumulation of wear debris, could be described as time and/or history dependent. According to Ludema, ”The probability of scuffing is not always the result of a simple additions of overloads or oil starvation that sliding surfaces may be subjected to”. Healing effects occur when the overload is removed, hence, the temporal spacing between overloads might be more important. Ludema used the term scuff quenching for the interruption of a progression towards failure [116]. With any of the hypotheses described, such quenching could occur. For instance if a surface film is formed, which reduces the shear stress; if wear debris is removed or if accumulated deformation of the subsurface is worn away. The latter is in line with the observation presented by Neale [114] and by engineers at MAN Diesel, where too low wear has been connected to a higher risk of scuffing.

One can think about it as a balance between worsening factors and healing factors and some type of transition is necessary for initiation of scuffing. Several researchers have described transformation to a state that can be considered as a prerequisite for scuffing, but that also can be healed. Dyson called it mild scuff [125], Ludema micro scuffing [116], while engineers at MAN Diesel call this micro seizure (see **Paper IV** and *Figure 26*).

5.4.9 Scuffing as destruction of lines of defence

Many of the presented theories have been shown to have value in specific areas. However, it is likely that scuffing is more complex and involves more than one of the mentioned mechanisms. Scuffing can be seen as a gradual destruction of the tribosystems *lines of defence* [117, 149]. The lines of defence that provide the scuffing resistance of the tribosystem are: the lubricating film, the formed tribofilm and the material itself. The mechanisms presented through the years are generally based on loss of one of these functions, but perhaps all of them need to be considered to understand scuffing.

In *Figure 27*, a schematic of the possible lines of defence are seen together with a number of parameters that affect and transform them. If a critical event takes place, one or several of the lines of defence can be changed and/or removed. If such changes occur to close in time and/or space, an aggravating situation can start and lead to a shift towards an unstable situation, which is the initiation of scuffing. If instead the lines of defence are recovered, the system can be transformed back to a stable condition.

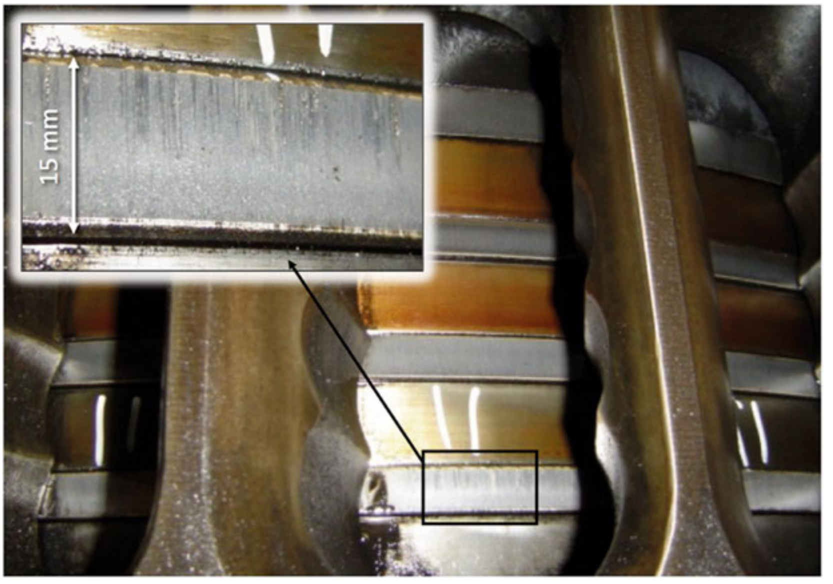


Figure 26. View of the 4 piston rings through the scavenge port of a marine 2-stroke engine. Micro-seizure, which could lead to a scuffing situation, is seen as the stripy appearance on the upper part of ring number 4 (see inset).

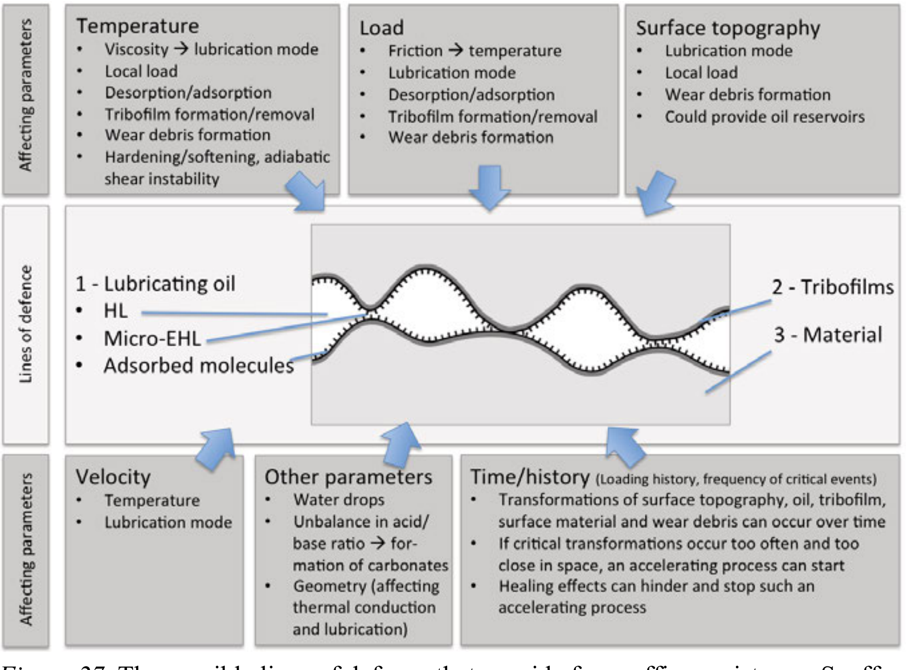


Figure 27. The possible lines of defence that provide for scuffing resistance. Scuffing can be seen as gradual destruction of these. Examples of affecting parameters are also shown together with parameters that are connected to them.

5.5 Experience of scuffing in engines

As discussed earlier, it is important to consider the application in question, even if full scale testing is not always possible.

In 1970, Neale tried to understand general scuffing performance patterns by studying performance of 83 internal combustion engines in a wide range of sizes [114]. It was thereby "possible to view them as a range of scale models". From this, it was clearly indicated that high piston speeds tend to make engines more prone to scuffing, while high mean effective pressure did not seem to be as important.

An interesting experience from engine builders in Neales study is that they did not think that an engine with scuffing problems could be cured only by increasing its oil consumption, but at the same time, attempting to decrease the oil consumption could lead to serious scuffing problems. Hence, too little oil is troublesome, but plenty of oil is not always enough to avoid scuffing problems.

Also according to Neale, there is evidence that scuffing is avoided in situations with a high wear rate of the cylinder. He suggests that it might be due to a completely different wear mechanisms taking place or, possibly, if formation of specific surface layers are important for initiating scuffing, there might not be enough time for this due to the high wear rate.

According to observations at MAN Diesel, the temperature of the cooling water for the cylinder have been observed to increase by 1-1.5°, 10-20 h before any visual signs of scuffing. Their experience is that scuffing problems can occur when (see **Paper IV** for further information):

- Water droplets in the scavenge air that condense on the cylinder liner destroy the oil film.
- The cylinder wear rate is too low, which can lead to a situation where the graphite flakes of the grey iron become closed.
- The liner surface becomes very smooth due to mechanical "bore polish" by a hard, calcium-containing layer on the piston. The layer is formed when excessive dosage of cylinder oil is used. Introducing a piston scraper ring in the liner, which removes this layer, solved the problem with bore polishing. However, problems with increased risk for scuffing still occur when excessive dosage of cylinder oil is used. It seems as if there are other negative effects of using excessive oil.

5.6 Scuffing resistance of materials

Optimisation of sliding materials for reduced risk of scuffing in marine engines is important to ensure well functioning engines operating on fuels with

low or no sulphur content. But how can a material's scuffing resistance be evaluated when scuffing is not fully understood?
It is widely accepted that scuffing depends on the materials in the sliding contact pair. But Ludema [116] stated in 1984 that:

> Whereas the material specialist does not give specific rules whereby a scuff-resistant material may be developed, he can often specify a rank ordering of materials in terms of scuff tendency for specific applications

This situation seems to be the same to this day. Further, the rank order was different for different applications and did not correlate with any specific material property [116, 118]. In a review paper by Scott et al. from 1975, material and metallurgical aspects of piston ring scuffing is discussed [118]. They emphasized the need for better understanding of scuffing mechanisms.

Through the years, numerous types of tests have been used to test scuffing resistance of materials as well as to investigate scuffing mechanisms. Several different configurations have been used, including ball-on-flat [105, 150], block-on-ring [139, 151], flat-on-flat [136] and ring/liner segments [152]. In **Paper III-V** of this thesis, ring segments as well as flat samples mating flat samples were used to get relevant surface pressures.

The sliding contact has to be aggravated somehow for scuffing to occur. This can be done by increased speed [105] or load [139, 150, 152], or by using only a small amount of lubricant [136, 151], so called starved lubrication. The two latter were evaluated in this thesis.

In most scuffing tests, increased friction and a specific coefficient of friction limit is used as scuffing criterion. Such a criterion was used in this thesis (as exemplified in *Figure 28*). However, other approaches exist. Qu et al. reported that the averaged coefficient of friction (averaged over the stroke in a reciprocating test) was not a sensitive enough criterion and instead used a specific increase in local coefficients of friction as scuffing criterion[153]. Blau et al. used a multiple criteria approach [154], whereas Saeidi et al. have used acoustic emissions, and was thereby able to detect scuffing initiation 5 minutes before the average coefficient of friction increased [155].

5.6.1 Testing scuffing resistance – contributions

In **Paper IV**, the potential of material selection based on lab scale scuffing tests was investigated. Test equipment and procedures used for the experiments were developed within the project (described in **Paper V**).

When tests were performed with step-wise load increase, it was impossible to reach an increased coefficient of friction, which is commonly used as a criterion for scuffing. Even at the maximum load of the experimental set-up used (1400 N), nothing happened as long as there was enough oil surrounding the contact. This load corresponds to a nominal surface pressure of roughly 350 MPa, which is much higher than the 5 MPa experienced by the top ring at typical combustion pressures in marine engines. To avoid testing a different wear mechanism than that present in the engine, we chose to move forwards with starved lubrication tests (see *Figure 28*).

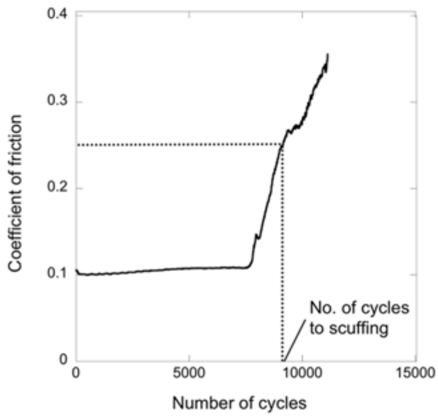


Figure 28. Typical friction curve from the scuffing tests at starved lubrication. The friction is low and stable for thousands of cycles, before it rises steeply and never falls back to the low level. A coefficient of friction limit of 0.25 was used as scuffing criterion.

The starved lubrication tests were performed after a preceding 40 000 cycle running-in period in flowing oil. Two piston ring materials were tested, grey cast iron and a plasma sprayed (PS) cermet coating (containing Ni, Cr, Cr-carbide, Mo), both currently used in engines. Piston ring samples were cut from rings removed from an engine and tests were performed with two different surface preparations. The surfaces were either left untouched, i.e. as when running in the engine (called field worn), or the surfaces were finely ground (called finely ground). In both cases flat grey iron samples, cut from a real cylinder liner, were representing the cylinder liner.

The ranking of the materials to depended on their surface preparation and the opposite ranking was achieved with the two different surface preparations (see *Figure 29*). The field worn samples are naturally more similar to the situation in the engine and is perhaps more reliable. With this surface preparation, the plasma sprayed coating slightly better. However, there was high scatter in the results, so any solid conclusion is difficult to make. High scatter in scuffing tests has been reported also by other researchers [136]. For this reason, many repeated tests are needed to give reliable results from scuffing testing.

In **Paper V**, further scuffing tests were performed, aiming towards finding new better performing piston ring materials. Two candidate materials were tested, Stellite 6 and a high-velocity-oxygen-fuel (HVOF) cermet coating. The HVOF cermet is also a sprayed coating, with the same constituents as the plasma sprayed cermet currently used in engines (Ni, Cr, Cr-carbide, Mo), but more dense and with lower porosity. The candidate materials were compared with the currently used materials, tested in **Paper IV** (results in *Figure 29*). In these tests, finely ground surfaces were used.

The scuffing resistance for the four materials is shown in *Figure 30*, where the results from the finely ground grey iron and PS cermet are shown again for easier comparison. The Stellite and the HVOF cermet performed somewhat better than the currently used materials, but also here, scattering is large. Further on, these tests had to be performed with finely ground surfaces, since field worn surfaces are difficult to obtain for candidate materials. The results presented in **Paper IV** indicated that this type of surface preparation might not be ideal, since the rank order was opposite compared with tests performed with field worn ring samples. Ideally, a surface preparation that leaves a similar surface characteristic as that found in well functioning engine should be developed for these types of scuffing tests.

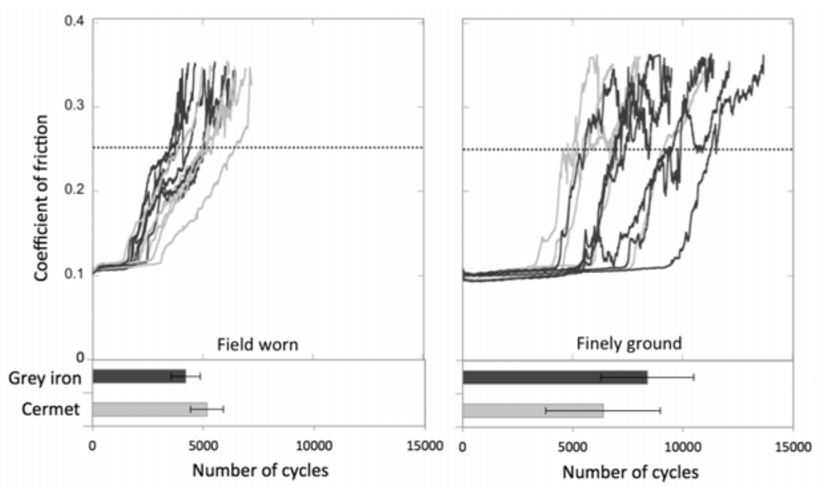


Figure 29. Scuffing resistance in tests with starved lubrication. Friction curves from 5 tests of each material/surface preparation combination are shown in upper part. Mean values and standard deviation for number of cycles to pass the scuffing on μ=0.25 in lower part.

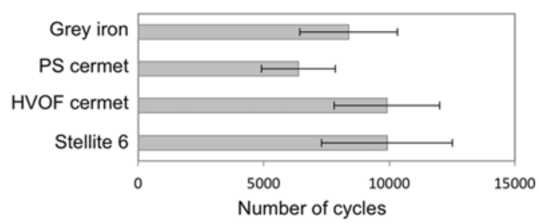


Figure 30. Mean values and standard deviations for number of cycles to scuffing for the four evaluated piston ring materials (μ=0.25 is used as scuffing criterion).

Further, unpublished findings from scuffing tests with starved lubrication indicate that grey iron with more open graphite lamella had higher scuffing resistance than grey iron with more closed lamella (see *Figure 31*). These results confirm observations in engines (described in section 5.5). These tests were performed with field worn samples with graphite characteristics that differed on different parts of the ring. The test procedure differed somewhat from the other tests presented here, both starved lubrication and a stepwise load increase was used in these tests.

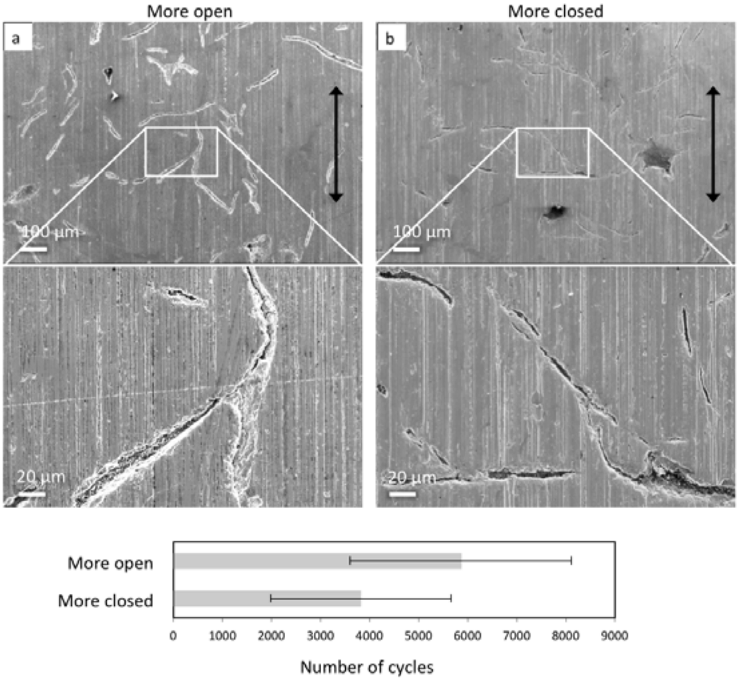


Figure 31. Mean values and standard deviations for number of cycles to scuffing for grey iron with more open a) or more closed b) graphite lamella. (μ=0.25 is used as scuffing criterion). SEM.

Concluding remarks on testing of scuffing resistance

The initial surface character was important for the scuffing resistance in the tests. When two piston ring materials were tested, the ranking between them depended on the surface preparation.

Further studies are needed to ensure that the material ranking in a specific lab test can be reliably transferred to engine performance. This motivates the investigations on mechanisms for scuffing initiation presented in the next section.

5.7 Contributions on scuffing mechanisms

After almost a century of research on attempting to understand scuffing criteria and mechanisms, it is relevant to ask if further studies can add anything. I believe that new advances in tribology as well as in high-resolution microscopy can help us to achieve further understanding of the surface modifications and transitions occurring at initiation of scuffing. For instance, the recent findings by Scherge and co-workers (described in section 2.2.5) helped to understand prerequisites for ultra-low wear rate. It gives us clues also about scuffing, which can be considered as the opposite to ultra-low wear. The findings in this thesis can be regarded as further puzzle-pieces and/or strengthening of existing ones.

In **Paper IV and V**, focus was on the mechanism on scuffing initiation in the tests.

5.7.1 Wear debris leading to oil depletion

In **Paper IV**, one conclusion was that oil depletion, due to oil being adsorbed by wear debris, was a crucial part of scuffing initiation in the lab tests (see *Figure 32*). Scuffing only occurred when the oil had been removed from the contact; In tests with much higher surface pressures than those present in engines, the sliding surfaces were still smooth and friction was stable as long as there was enough oil in the contact (see *Figure 33*). Thus, scuffing did not occur as long as there was oil in the contact. The influence of wear particles for scuffing initiation is in line with the theories presented by others [145-147].

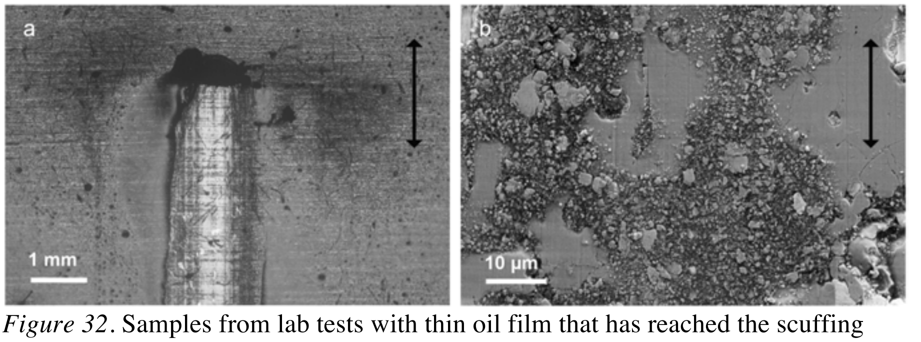


Figure 32. Samples from lab tests with thin oil film that has reached the scuffing criterion. (a) Scraped off wear debris at turning point of wear mark on grey iron sample representing the liner. The wear mark itself has no visible signs of oil after the test. Light optical microscopy. (b) Example of agglomerated wear debris. A mixture of small and relatively large wear particles fills pores and cavities of a cermet sample, representing a piston ring in the lab test. This wear debris originates mainly from the mating grey iron. SEM, EDS used to confirm elements.

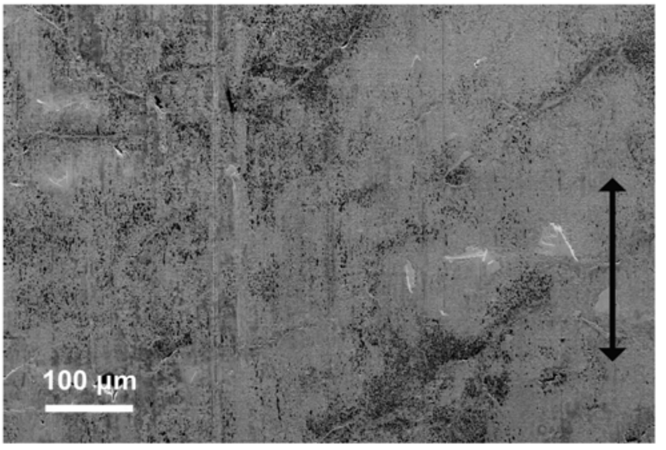


Figure 33. Example of the smooth surface of grey iron sample representing a piston ring in a test with final load of 1400 N and oil surrounding the contact during the whole test. The darker areas contain additive elements from the oil. The graphite lamellas were closed over the whole wear mark, but neither roughening of sliding surfaces nor increased coefficient of friction was obtained, i.e. no scuffing occurred. SEM, EDS used to confirm elements.

How is this relevant in the engine? Could accumulation of wear debris be an initiating factor just as in these lab tests? This question could be answered by performing studies on piston rings that are removed when scuffing has just started.

We know from experience in marine engines that the temperature of the cooling water increases before any visual signs of scuffing. It is probable that an increased friction force causes this temperature rise. In **Paper IV**, different causes for increased friction are discussed. An accumulation of wear particles in the contact was one possible cause. This could affect either the degree of BL, the friction level in BL parts of the contact and/or lead to local load concentration.

5.7.2 Scuffing as a process of several stages

The mechanisms behind scuffing initiation in the lab test were further investigated in **Paper V,** where scuffing tests were performed with four different piston ring materials.

There was a variation in characteristics of the failed surfaces, both between different locations on the same sample, but also between samples of the same ring material as well as between samples of different ring materials. A number of recurring characteristic features could be identified. An example of their distribution on the sliding surfaces is shown in *Figure 34* and in *Figure 35* SEM-micrographs exemplifying these features are shown (the same letter denotation is used in the two figures, although the examples are not necessarily coming from the same sample).

The results indicate that scuffing occurs in several stages with separate mechanisms and that these can be active simultaneously at different locations of he sliding surface. This shows that small surface variations can lead to large changes in local performance. Local transformation of the surface leads to an aggravated situation in nearby areas, and consequently to the stripy appearance.

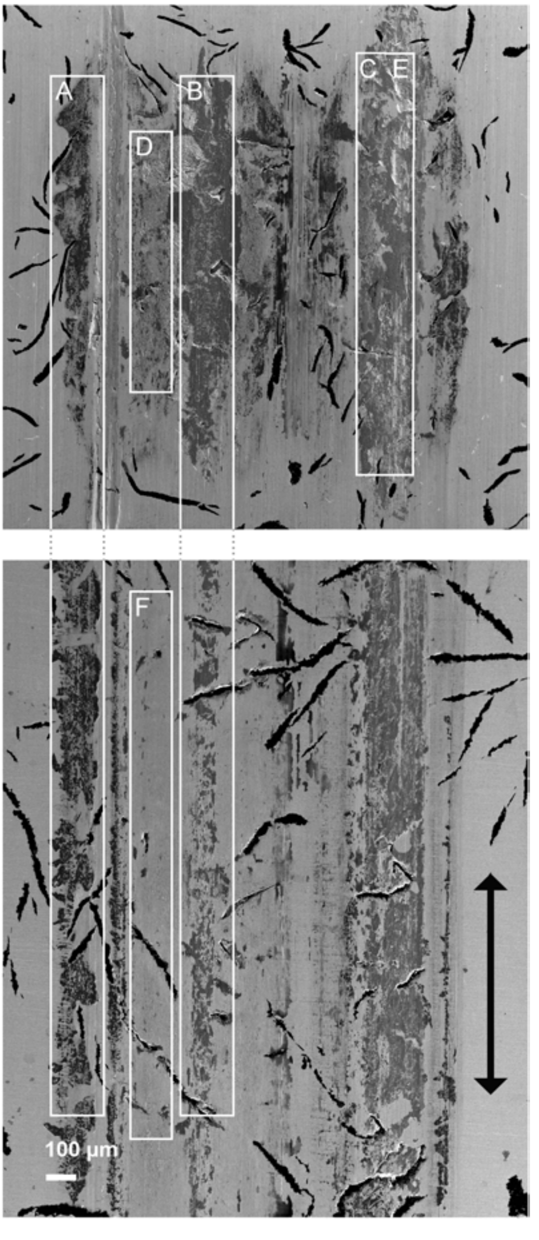


Figure 34. Example of wear mark appearance on grey iron sample representing piston ring (upper) and mating grey iron sample representing cylinder liner (lower) (sliding direction is vertical in the micrographs). The boxes frame examples of the different characteristic features described and exemplified in Figure 35. They also indicate that the features on the ring match those on the corresponding surface positions on the liner. SEM.

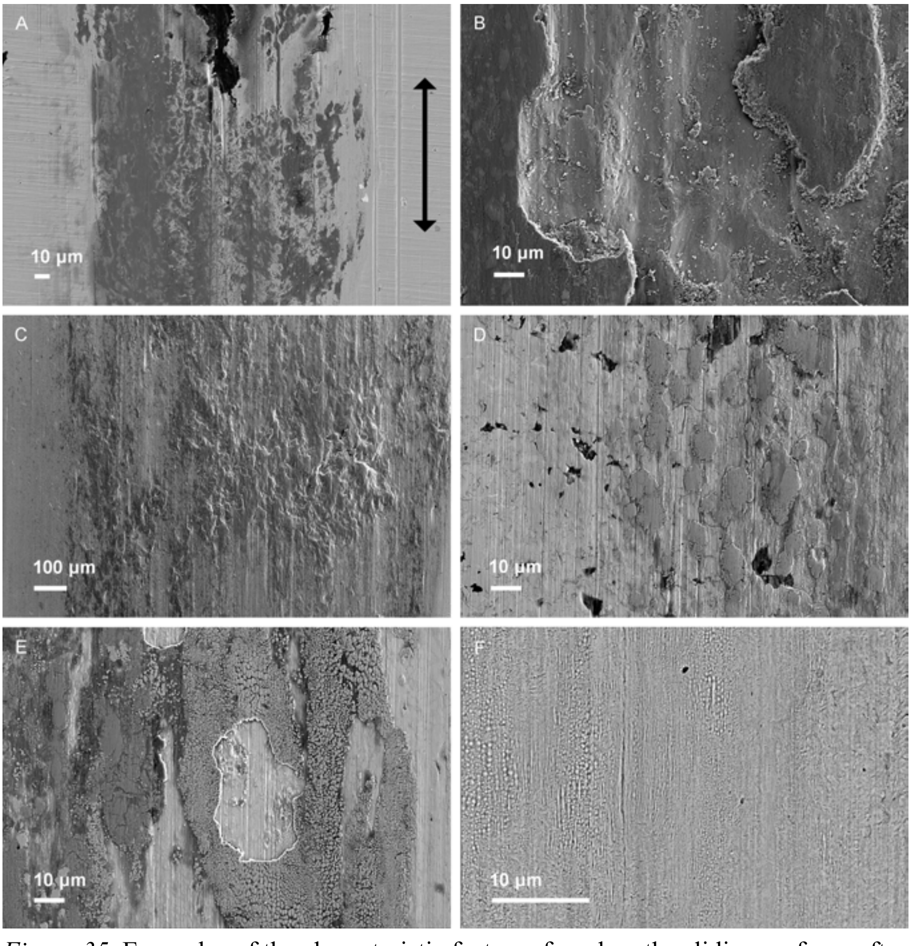


Figure 35. Examples of the characteristic features found on the sliding surfaces after tests reaching the scuffing criterion. The examples shown are from tests with different ring materials. SEM at different magnifications.

A) Tribofilm (darker grey) containing Fe, O, Ca, C and S, here on liner sample.

B) Agglomerated wear debris. In this example, partially sintered fine debris.

C) Roughened surface. This is one of the worst examples on a ring sample.

D) Iron (medium grey) transferred from liner samples.

E) Spalling of transferred material, revealing (brighter) underlying ring surface.

F) "White layer", found in areas of the liner sample corresponding to areas with transferred iron on the ring (see D).

Based on the presented characteristic features, a hypothesis for the initial stages and mechanisms of scuffing failure was proposed. Further details are found in **Paper V**, but a short version is presented here:

1. Tribofilm is formed and the wear rate is low during well lubricated sliding.
2. Wear and agglomeration of wear debris during local starved lubrication aggravate the situation because the amount of oil is reduced as oil is adsorbed by wear debris. Increased adhesion and friction because of oil starvation lead to increased temperature.
3. Locally, iron is transferred from the liner sample to the ring sample and white layer is formed on the liner sample.
4. Spalling of transferred material, roughening of surface and formation of large wear debris. Aggravation of the situation locally, which eventually lead to larger areas with aggravated oil starvation and wear.

Both the influence of wear particles on scuffing initiation and the formation of a white layer before scuffing is in line with some of the literature reviewed in section 5.4.

No attempt was made to classify the mechanism behind wear during scuffing, focus was rather to look at a wider perspective and try to understand the whole chain of events. The theories based on low cycle fatigue, adiabatic shear instability and critical shear stress could all be part of the wear mechanism as observed in our research.

5.7.3 Concluding remarks on scuffing mechanisms

The main conclusions on scuffing mechanisms in this thesis are that in the lab tests performed with thin oil film of fully formulated cylinder oil:

- Scuffing does not occur as long as there is enough oil in the contact.
- Accumulation of wear debris plays a role for impairment of lubrication.
- Scuffing is a process of several stages.

These conclusions support some of the previous findings on scuffing mechanisms. Further studies are needed to confirm if these findings also are important for scuffing initiation in the engine. Especially, the effect of wear debris on the lubrication situation is interesting as a part of the initiating scuffing mechanism. Wear debris could work as an impairing factor during the whole scuffing process, which means that healing will be difficult once the process has started. Thereby, we have a possible explanation for a transition that is difficult to come back from even if more oil is added.
Interesting questions include whether some aspects of the scuffing process are more important for the performance of a specific material and whether we can use such knowledge to understand which material properties that are more important to focus on. For instance:

- If the wear rate of a specific ring/liner system is an important factor for scuffing resistance or if the ability of a material to retain wear debris is more important.
- How a materials ability to form a lubricating tribofilm or its ability to retain lubricating oil affect the scuffing resistance.
- Whether sulphur in the fuel have different effect on the scuffing tendency of different types of materials.

Further studies could include tests that are interrupted at different stages, preferably with samples that have specific differences in material properties. Microscopy investigations of subsurfaces in cross-sections and analysis of field samples showing signs of micro-seizure or scuffing could also be interesting.

6 Conclusions

The aim of this thesis is to increase the knowledge in two fields of tribological research, both targeting greener combustion engines. The first field involves the tribological mechanisms and possibilities of boric acid as an energy saving fuel additive. The most important conclusions can be summarised as:

- A test method to simulate the combined lubrication of boric acid fuel additive and ordinary engine oil in the piston-ring/cylinder-wall contact has been developed and evaluated. Several approaches were compared. The best method found with respect to stable friction behaviour and possibilities to perform long tests involves repeated spraying of a mixture of the fuel additive fluid and a small amount of base oil onto prelubricated sliding surfaces, at room temperature.
- Spraying boric acid fuel additive to a prelubricated surface results a in substantially reduced friction. A reduction by up to 78% compared with relevant references was achieved, as measured over the full stroke (in room temperature tests).
- The friction reduction depends on both load and frequency of motion (sliding velocity). At the lowest test frequencies, the friction was reduced by up to 89% at mid-stroke.
- The friction reducing effect is dramatic close to the turning points in the reciprocating motion. The friction falls down towards its low mid-stroke values much quicker than with the reference lubrication.
- By combining a set of assumptions, a scenario is presented that shows how the large efficiency improvements observed in field tests (6% in cars) could be explained by friction reduction in the piston assembly of the engine.
- The low friction obtained in lab tests with the boric acid fuel additive was ascribed to formation of tribofilms containing boric acid.
- Analysis of the tribofilms was complicated by their lack of long-time stability. This fact is not evident from earlier literature, but is of course a vital for future research in the area.

Secondly, focus is on a better understanding of scuffing mechanism and the possibility to test the scuffing resistance of sliding materials. These studies proved to be challenging. In fact, the mechanisms of scuffing have been studied for decades, but are still not well understood. However, these are examples of the conclusions that could be made:

- Regarding the expected positive effect of having the environmentally harmful sulphur in the fuel, there was no clear answer on whether this actually provides lower risk of scuffing. Surface analysis of field worn piston rings showed that the surface layer had no or a very low sulphur contents, which was expected to be a crucial part of any lubricating tribofilm associated to use of sulphur rich fuels.
- Scuffing resistance testing is difficult e.g. due to a large scatter in the results. However, two new candidate coatings: Stellite 6 and HVOF cermet (Ni, Cr, Cr-carbide, Mo), showed somewhat better results than the currently used piston ring materials.
- From lab tests, it was clear that scuffing is a process that occurs in several stages. A hypothesis for initiation of scuffing that includes impaired lubrication due formation of wear debris or other particles is presented.

7 Future work and outlook

Combustion of fossil fuels should be replaced by greener options and the fossil fuel demand should be reduced by changes in transportation and consumption behaviour. Nonetheless, it is likely that combustion engines will be used widely for the foreseeable future. A boric acid fuel additive could potentially enable immediate fuel savings in combustion engines all over the world. Boric acid is cheap, abundant in nature and its fuel saving effect does not require rebuilding or replacement of current vehicles. The effect is probably larger in urban driving, which includes a large percentage of low load driving and idling. Furthermore, by reducing friction and thereby protecting surfaces in boundary lubrication, the use of lower viscosity oils can be enabled. This could lead to decreased hydrodynamic friction losses, which are more important in highway driving.

The fuel additive could have further positive effects at operation on biofuels by protecting sliding surfaces that are subject to increased wear problems with these fuels, such as fuel injection devices. Additionally, the antiseptic effect of boric acid might prevent bacterial growth, which is otherwise a concern with the new biofuels.

In order to increase the knowledge further, the above-described effects should be studied. Further, the uncertainties around the estimations on potential fuel savings could be minimized, for instance by optimizing the tests at 100°C further or even better, by performing tests in fired engines that enable friction measurement with the floating liner or instantaneous IMEP technique. If such tests are combined with the radionuclide technique, the effects of boric acid on wear rate could also be investigated. An additional and important step forward is to investigate how well the additive works together with other additives commonly used in fully formulated engine oils. There is a risk that additives compete with each other.

Another important aspect is that of health risks. We know that many additives used in lubricants today lead to emissions of particular matter that are harmful upon inhalation. These emissions could potentially be reduced by the use of boric acid. However, it is imperative to also study the risk of inhaling relevant low concentrations of boric acid particles that will be part of the emissions if a boric acid fuel additive is used.

When it comes to scuffing in engines of cargo ships, upcoming regulations will probably lead to further insights into the risk of scuffing when operating on low sulphur fuel. In the best case, the concern for higher scuffing risk has been overstated and optimization of the amounts of neutralising agents in the fuel will be enough to provide well functioning engines. If scuffing will occur more frequently, this will of course be costly and have a negative effect on the shipping industry. However, in close cooperation with ship operators, it could also be an opportunity to study scuffing mechanisms of real engines as well as to test new piston ring materials. Especially, thorough studies of piston rings with so-called micro-seizure would be interesting. Similarly, it is probably valuable to study piston rings that have been removed from the engine just after the first signs of scuffing initiation has been detected. Without further studies of scuffing mechanisms in actual engines, it is difficult to confirm the relevance of any type of lab scale testing.

Nonetheless, to have further understanding of scuffing is also benefited by additional lab scale scuffing tests accompanied by analysis of surfaces, as well as sub-surfaces (cross-sections) at different stages of the scuffing process.

Finally, it would be interesting to join these two areas of research and study whether boric acid as fuel additive could prevent scuffing, as well as whether it could provide better fuel economy in the already fuel efficient cargo ships.

8 Svensk sammanfattning

8.1. Tribologi för grönare förbränningsmotorer

Denna avhandling handlar om *tribologi* som kan göra fordonstransporter miljövänligare. Men vad är tribologi, och vad har det att göra med miljön?

Låt oss börja stort med grundförutsättningen för allas våra liv. Miljön här på planeten jorden är en förutsättning för att vi ska kunna leva som vi gör. Det är de stabila förhållandena under den 11 700 år långa perioden *Holocen* som har möjliggjort utvecklingen av dagens samhällen [1]. Framsteg inom jordbruk, teknik och medicin är också några av hörnstenarna för våra globala moderna samhällen. Utvecklingen har varit snabb under de senaste århundradena, tyvärr inte bara av godo, då den också innebär påfrestningar på den miljö som vi lever i och av. Dessa påfrestningar har blivit kända för allmänheten under de 50 senaste åren och många räknar den amerikanska marinbiologen Rachel Carson som en av de viktigaste pionjärerna inom miljörörelsen. Hennes bok *Tyst vår*, kom 1962 och förklarade hur användningen av DDT påverkade vilda djur [2]. Sen dess har larm om miljöförstöring, både på lokal och global nivå, blivit en del av vår vardag. Lokalt kan det handla om surt regn som härstammar från industrier och fartygstransporter och som är skadligt för vår hälsa och för växter och djur i naturen, men också för byggnader och kulturarv. Globalt handlar det framförallt om utsläpp av växthusgaser som leder till global uppvärmning. Denna klimatförändring hotar stabiliteten i vår miljö och därmed också våra samhällen.

Tribologi är läran om ytor i glidande kontakt, läran om friktion, nötning och smörjning. Tribologi som koncept är inte nytt. Slädar som användes för att dra tunga stenar till pyramiderna i det antika Egypten smordes med vatten och för 500 år sedan studerade Leonardo da Vinci de grundläggande friktionsmekanismerna. Men det var för drygt 50 år sen som termen tribologi myntades för första gången i den berömda Jost-rapporten [3]. I denna uppskattades det bland annat att 28 miljoner pund skulle kunna sparas genom minskad friktion och därmed minskade energiförluster, bara i Storbritannien och Nordirland. Det här var innan det blev allmänt känt att vår miljö påverkas av användningen av fossila bränslen som energikälla. På senare tid är tribologi ofta kopplad till att lösa miljöproblem.

Ungefär 28 procent av bränsleåtgången i en bil beror på friktionsförluster [4]. Om vi minskar dessa förluster kan vi minska utsläppen av växthusgaser och därmed hejda den globala uppvärmningen. Även minskad nötning kan leda till minskad energiåtgång eftersom det går åt energi för att ta fram nytt material och nya komponenter när något går sönder. Det kan också vara så att en förändring för att minska farliga utsläpp *i sig* kan leda till tribologiska problem som måste lösas för att förändringen ska vara möjlig.

Helt klart är det att forskning inom tribologi liksom ny teknik i allmänhet kan leda till mindre miljöpåfrestningar per kilometer som en bil körs eller per transporterat ton gods. Men det är också viktigt att fundera över om tekniska lösningar är tillräckliga för att vi ska kunna leva inom hållbara gränser för vår planet. Utifrån forskningsresultat om miljövänliga transporter så har forskare kommit fram till att det *inte* är troligt att tekniska lösningar räcker för att vi ska kunna minska utsläppen av växthusgaser [5]. Det är även viktigt att minska vårt behov av transporter för att stävja de ökningar som är en följd av ekonomisk tillväxt. Det finns till exempel en risk för att bränslesnålare bilar leder till fler och längre resor och till att konsumtionen av andra varor ökar eftersom att det blir billigare att köra bil. Många forskare betonar därför vikten av att minska den totala efterfrågan av resurser, till exempel vad gäller transporter och konsumtion [5, 9].

Det finns en risk att tekniska lösningar kan förflytta fokus bort från andra angreppssätt som kan vara nödvändiga för att vi ska kunna behålla vår enda kända miljö för modernt liv. Detta betyder inte att tekniska lösningar inte också är viktiga steg framåt, och självklart är det fokus i denna tekniska avhandling. Här presenteras forskning som syftar till att öka kunskapen inom två olika områden. Dels för att öka förståelsen av den smörjande effekt som borsyra har när det blandas som bränsleadditiv och dels för att förstå de nötningsproblem som tros öka när man byter till miljövänligare bränsle i stora lastfartyg.

Forskningsarbetet har framförallt inneburit:

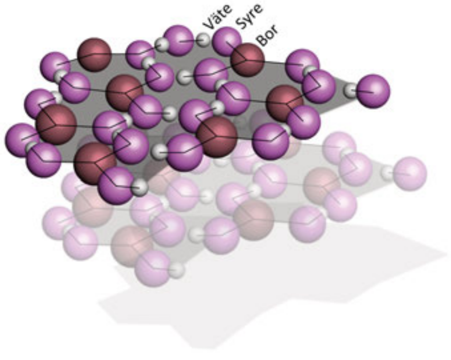
- studier av publicerad forskning som gjorts inom dessa och närliggande områden
- kommunikation med ingenjörer och forskare inom industrin för att få en bra förståelse för de erfarenheter som finns inom olika områden
- utveckling och evaluering av testutrustning och testmetoder
- labbtester för att förstå tribologiska mekanismer och hur dessa påverkas av olika parametrar
- avancerad ytanalys för att förstå tribologiska mekanismer, dvs. vad som verkligen händer på ytorna under den glidande kontakten

8.1.1 Borsyra för minskad bränsleförbrukning i motorer

I test med bilar, lastbilar och diselgeneratorer har man sett att bränsle kan sparas om man tillsätter en produkt som innehåller borsyra till bränslet [75, 76]. Borsyra är ett ämne som är billigt eftersom det finns gott om det; och det är även relativt ofarligt. En sådan produkt skulle snabbt kunna introduceras för bilar och andra transporter som används i världen idag, vilket möjliggör direkt minskning av fossila bränslen. En del andra förbättringar som görs för att minska energiförluster innebär att bilar måste bytas ut eller göras om, vilket av förklarliga skäl sker på längre sikt. Vårt arbete har syftat till att verifiera den friktionssänkning som kommer från att använda borsyra som bränsletillsats samt att förstå hur och när en sådan produkt fungerar som bäst.

Vi har utvecklat en testmetod för att försöka efterlikna de förhållanden som finns i cylindrar på motorer. Vi såg en stor minskning av friktionen i ett antal test där vi på olika sätt tillsatte borsyra till en oljesmord glidande kontakt. Det mest stabila testet fick vi då vi med jämna mellanrum sprayade borsyra på en glidande oljesmord kontakt. De största sänkningar som vi fick av friktionens medelvärde var 50 procent. På en del ställen av provet var friktionskoefficienten så låg som 0,02 under stora delar av testet, vilket innebär en friktionssänkning på 75 procent. Om man antar att denna friktionssänkning skulle ske även i liknande kontakter i motorn så har vi uppskattat att det skulle kunna leda till en minskning av bränsleförbrukningen på 3,6 procent. Det finns stora osäkerheter i en sådan uppskattning, men faktum är att ännu större minskningar i bränsleförbrukning har setts i fälttester.

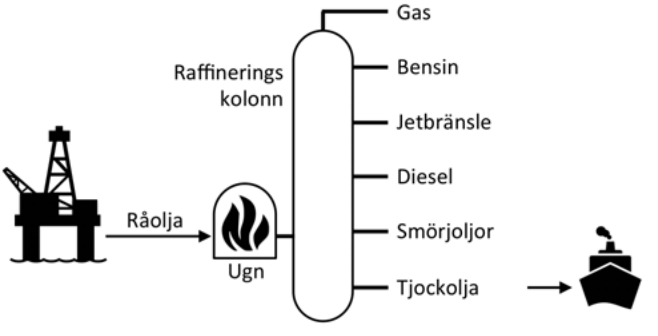
Det är sedan tidigare känt att borsyramolekylerna ligger i en lagrad struktur och att det kan ge låg friktion [61]. Lagren har starka kemiska bindningar inom sig, medan det är svaga bindningar mellan lagren (*Figur 36*). Detta leder till att de lätt glider längs med varandra. Ett tunt skikt av sådana lager ovanpå en hård yta, exempelvis en motorkomponent, ger låg friktion. Våra analyser visade att utseendet på skiktet berodde både på hur borsyra tillsattes och på temperaturen. En viktig insikt för vidare studier var att de bildade skikten inte var stabila över tid. Tyvärr försvårade detta ytterligare analyser.



Figur 36. Borsyra har en lagrad struktur. Varje lager består av plana borsyramolekyler med starka bindningar mellan atomerna medan de är svaga bindningar mellan lagren. Detta gör att de glider lätt mot varandra.

8.1.2 Nötningsproblem väntas öka med miljövänligare bränsle

För att minska utsläpp av svavelhaltiga avgaser och därmed minska mängden surt regn så finns det planer på att byta bränsle i stora lastfartyg. En tanke är att de ska drivas på naturgas i stället för det bränsle som används idag, den svavelrika tjockoljan som är en restprodukt vid oljeraffinering (*Figure 37*). I fartygsindustrin finns det dock erfarenheter av att risken för den katastrofala typen av nötning som på engelska kallas *scuffing,* ökar om man använder bränsle med mindre svavel. Då skuffning (mitt förslag på svensk översättning) sker förstörs komponenter helt och hållet och måste bytas ut. Detta är både dyrt och tidskrävande och kan dessutom medföra säkerhetsrisker om fartyget är långt ifrån land.



Figur 37. Den billiga svavelrika tjockoljan är en restprodukt som bildas då andra typer av oljor och bränslen destilleras från råolja. Tjockoljan används vanligen som bränsle i fartyg.

Arbetet i den här avhandlingen har inriktats på att förstå varför den risken ökar, huruvida man i enkla labbtest kan avgöra vilka kolvringsmaterial som motverkar den ökade risken för skuffning; samt på att bättre förstå mekanismerna bakom nötningsproblemet.

Utifrån resultaten var det svårt att påvisa mekanismen bakom den positiva effekten av svavel i bränslet. Svavel kunde inte detekteras på kolvringarnas ytor, så som förväntat om svavel är del av ett fast smörjande skikt. Däremot bildades svavelinnehållande skikt i labbtest och det hittades även på ett prov som borrats ut ur cylindern som kolvringarna glider mot i motorn. Svavel kan alltså vara med och forma tribofilmer. Resultaten visade också att det blir högre svavelhalt i skikt som bildats med olja som tappats ut från en motor och därmed innehåller svavel även från bränslet.

Vad gäller möjligheterna att jämföra hur olika kolvringsmaterial står emot skuffning så visade det sig att rankingen mellan olika material kan påverkas av hur ytorna prepareras. Det var också en stor spridning i resultaten, vilket innebär att det är svårt att dra några starka slutsatser om vilka material som är bäst. De nya material som testades presterade dock något bättre än de material som används idag och kan därför rekommenderas för vidare tester i riktiga motorer.

Svårigheten att jämföra olika materials motstånd mot skuffning är inte helt oväntad eftersom man inte riktigt vet vilka mekanismer som ligger bakom nötningsproblemet. Därmed vet man inte heller vilka mekanismer som är viktiga att återskapa i ett labbtest. För att öka förståelsen för dessa mekanismer analyserades ytorna efter testerna. Bland annat kom vi fram till att skuffning inte skedde så länge det var olja i kontakten och att det verkade som om oljan försvann genom att sugas upp av nötningspartiklar för att sedan knuffas bort från kontakten. I testerna var det också tydligt att skuffning sker i flera steg med separat mekanismer. En hypotes för hur skuffning kan gå till föreslogs men ytterligare studier behövs för att avgöra om denna hypotes är relevant för vad som händer i motorn.

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