

Task 62: Wear in Engines Using Alternative Fuels

Main report

Jesper Schramm

Editor

September / 2024

Preface

It has been established that most alternative fuels behave differently when applied to state of the art combustion engines for traditional fuels. Of concern are different wear issues that have shown to be caused by these new fuels.

The IEA Advanced Motor Fuels (AMF) Technology Collaboration Program (TCP) has initiated this task in order to get an update on the knowledge about wear in combustion engines, caused by application of alternative fuels. This report is thus the main report of AMF TCP Task 62: "Wear in Engines using Alternative Fuels". The report has been written and the work has been carried out in collaboration with the Advanced Materials for Transportation (AMT) TCP.

The countries in AMF and AMT that have contributed to the work are: Brazil (AMT), China (AMF), Denmark (AMF), Finland (AMF) and Germany (AMF). Furthermore USA (AMT) has contributed with information about lubrication in electric motors. However, this topic is more seen as relevant for future collaboration.

The report here is based on a general literature review carried out by Denmark, and individual reports from the member countries of Task 62. The work of AMT TCP is reported in [0-1]

The following reports have been published under Task 62 [0-2,0-3,0-4]:

Task 62: Wear in Engines Using Alternative Fuels.

Main report

Edited by Jesper Schramm.

Authors:

Brazil: Henara Costa, Roberto M Souza – IEA Advanced Materials for Transportation TCP (chapter 5.1)

China: Wei Anli (chapter 5.2)

Denmark: Jesper Schramm (chapter 1,2,3,4,6,7,8,9)

Finland: Pävi Aakko-Saksa, Taina Ohra-aho, Anja Oasmaa, Carolin Nuortila (chapter 4)

Task 62: Wear in Engines Using Alternative Fuels .

Wear associated with application of methanol in combustion engines - Chinese experiences

Edited by Wei Anli

Task 62: Wear in Engines Using Alternative Fuels.

The influence of fuel H/C ratio on engine wear

Denmark: Rune WK Christensen, Jesper Schramm

Germany: Fanny Langschwager, Ulrike Schuemann, Bert Buchholz

Summary / Abstract

Alternative fuels have been intensively introduced in transportation sectors in recent years. While some of the wear caused by these fuels can be seen initially, the problems really become clear after years of application. The goal of this task was to identify and present an overview of potential wear issues to prevent major surprises in the future.

The Task evaluated excess wear in internal combustion engines caused by the use of alternative fuels. The objectives were to review ongoing related projects in the member countries and conduct a general literature review to evaluate which engine wear problem that can be foreseen with future application of alternative fuels.

The key questions to be addressed were as follows:

- How severe are the problems associated with use of alternative fuels?
- What is the expected increase in engine wear caused by these fuels?
- What can be done to solve these problems?

For biofuels suitable for diesel combustion the major problems are associated with dilution of lubricant with fuel, the fuel tends to biodegrade, and corrosive nature is seen towards some materials.

For ethanol, wear conditions are worsened due to lowering lubricant viscosity and due to water content in the lubricant. Ethanol, furthermore, reacts with the lubricant. This increases the acidity of the lubricant and the breakdown of some lubricant additives. On top of this, increased water content of ethanol, which is often seen, increases engine corrosion.

For methanol, the same issues as for ethanol with water is seen. Chinese experiences conclude on more specific material issues which are summarized in Table 6. Furthermore, formation of formic acid has a negative impact on anti-wear performance. Methanol, lubricant and water forms an emulsion at low temperatures which can cause lubricant to fail. Lubricants need improved alkali values and antioxidant properties for the engines to work properly. Finally, spark plugs undergoing pitting and ablation is seen.

Hydrogen is reported to cause surface embrittlement, fuel injector failure (due to bad lubricity) and prevention of formation of surface protective oxides. Furthermore, hydrogen is seen to decrease lubricant additive content in many different ways, and it can cause emulsification of the lubricant. Finally, excessive wear is caused by water condensation on the cylinder liner.

Ammonia is a relatively new fuel for combustion engine applications. Therefore, much more experience is needed to describe the fuel impact on wear completely. However, corrosion effects on copper alloys are reported, and it is expected that this is also the case for other materials. Increase in lubricant viscosity has been reported, caused by amines, and high water content in the exhaust is expected to cause excessive wear due to water condensation on the cylinder liner.

DME was seen as a highly relevant potential fuel to substitute diesel in the early 2000's. The problems with DME is that it is an excellent solvent which can cause damage to most materials. However, materials resistant to DME have been identified due to huge interest in applying DME in the early 2000's. DME's low lubricity has caused surface wear in the fuel injection system. Additives have been developed to mitigate this problem.

Authors

Brazil:

Henara Costa, Roberto M Souza

IEA Advanced Materials for Transportation TCP (chapter 5.1)

China:

Wei Anli (chapter 5.2)

Denmark:

Jesper Schramm (chapter 1,2,3,4,6,7,8,9)

Finland:

Pävi Aakko-Saksa, Taina Ohra-aho, Anja Oasmaa, Caroline Nuortila (chapter 4)

Content

1. Introduction	5
2. Tribology	6
3. Wear in internal combustion engines	9
4. Natural oils, biodiesel and bio-oils	13
5. Alcohols	20
5.1 Ethanol	20
5.2 Methanol	27
6. Fuels with high hydrogen content.	29
6.1. Methanol	29
6.2. Ammonia	29
6.3. Hydrogen	30
6.4. DME	30
6.5. The influence of fuel H/C ratio on engine wear	31
7. Conclusions	33
8. References	35

1. Introduction

Electric Vehicles (EV's) are gaining more volume in road transportation in these years, mainly due to Green House Gas (GHG) emission concerns. The plan, in many countries, is to phase out the use of gasoline and diesel fuels in road transportation. However, the traditional fuels cannot be replaced by electricity in all practical cases, and the solution here could be application of alternative carbon neutral fuels, like biofuels and e-fuels.

These fuels have already been introduced in many applications, but today the application volume is limited compared to gasoline and diesel. This is, however, foreseen to change much in the future few decades. Therefore, the wear issues that have occurred during application of other (alternative) fuels in traditional engines must be addressed now, before the introduction of these fuels accelerate fast.

So far, we have quite much experience with application of bio-oils, methanol and ethanol in combustion engines. This is also reflected in this report, where the reported sections of these fuels are well covered compared to other relevant alternative fuels like DME, hydrogen and ammonia. The experiences concerning engine wear with these fuels will be expanding in the coming years as the application is seen to a wider extend. However, a common feature of these fuels are the increased hydrogen to carbon ratio, H/C, which in this investigation has been found to be of major importance in relation to engine wear.

2. Tribology

Tribology is the common name for the phenomena of friction, wear and lubrication. These phenomena are strictly connected in a machine.

Wear, which is the topic of this report, is thus related to friction and lubrication. The consequences can be strengthened by other factors like the chemical environment. It is therefore appropriate to explain these phenomena, which are the background for wear in engines.

Friction

Friction can be defined as the physical resistance to relative motion at two or more surfaces in a state of mutual contact. Usually in machinery the surfaces are not in direct contact, but more or less separated by a lubrication layer with the purpose to reduce friction. We are talking about different types of contact:

Gas friction

A gas layer completely separates the object and the opposed body from one another.

Fluid friction (hydrodynamic and hydrostatic friction)

A fluid layer completely separates the base object and opposed body from one another.

Combination friction

The base object and the opposed body are in mutual contact at surface peaks. The friction load is shared by lubricating film and by the objects in contact.

Dry or boundary friction

The lubricating film no longer performs any support function, but residue from previously absorbed lubricants continues to exercise a tribological effect.

Solid body friction

Direct contact between the opposed surfaces.

The most significant physical parameters for describing friction are:

- F , the friction force, which is the force required to move the bodies
- P_f , the friction power, which is:

$$P_f = F \times V_{ss}$$

where V_{ss} is the sliding speed.

- C_f , the coefficient of friction, which is the friction force relative to the normal force.

Lubrication

There are four lubrication regimes - boundary, mixed, elastohydrodynamic and hydrodynamic.

The coefficient of friction for the four regimes are shown in the figure below as a function of the specific film thickness, λ . The specific film thickness is defined as: the ratio of the

minimum film thickness (h_{\min}) to the composite surface roughness of two surfaces in contact.

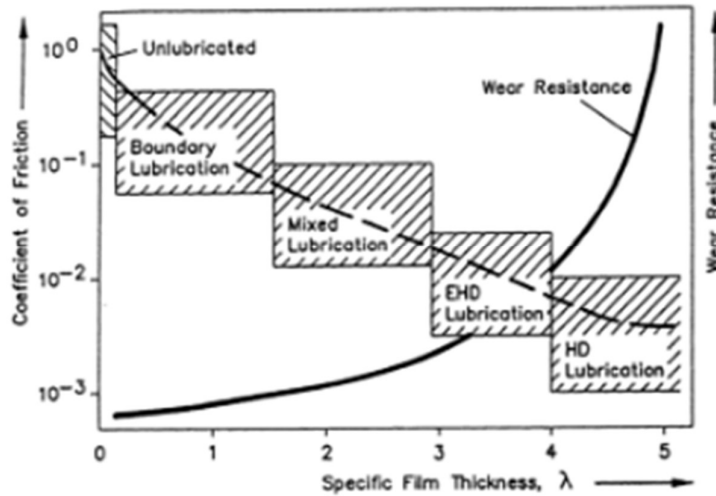


Figure 1. Coefficient of friction and wear resistance as a function of the lubrication regime [2-1].

Boundary lubrication

Boundary lubrication is associated with metal-to-metal contact between two sliding surfaces of the machine. The metal surfaces in a lubricated system in this regime may actually come into severe contact with each other. If the oil film is not thick enough to overcome the surface roughness of the metal, a lambda value of less than one results.

We generally want to avoid boundary lubrication where possible. It is agreed among lubrication specialists that friction may be at its highest level during the boundary lubrication regime. This occurs at start-up, shutdown, low speed or high load conditions. Boundary lubrication regimes occur during any condition where the asperities of two lubricated surfaces in relative motion may come into physical contact and the potential for abrasion and/or adhesion occurs. A main method of reducing boundary lubrication is to provide the correct lubricant viscosity. A lubricant with too low of a viscosity cannot keep the metal surfaces separated, and metal-to-metal contact occurs. A secondary method of reducing this phenomenon of the boundary lubrication regime is with the use of a fully formulated lubricant that includes anti-wear or extreme pressure additives.

Mixed film lubrication

Generally speaking, boundary lubrication is dramatically reduced as sliding speed increases, creating a wedge of lubricant film between the surfaces in motion. As the potential for asperity contact is reduced and film thickness is increased, the coefficient of friction drops dramatically to the condition known as mixed lubrication. Some metal-to-metal asperity loading is still occurring combined with loading (lift) on the lubricant. This is an intermediary condition between boundary and hydrodynamic/elastohydrodynamic lubrication regimes. As the oil film thickness increases further, the system now moves into full film lubrication, either elastohydrodynamic or hydrodynamic lubrication.

Hydrodynamic (HL) lubrication

This lubrication regime condition occurs after a machine has begun to operate and the speeds and loads are such that a wedge of oil has been formed between the surfaces. We also call this full film lubrication. This is a desirable condition to avoid friction and wear. Any friction remaining is found within the lubricant itself, as the molecular structures of the oil slide past each other during operation. Oil films are typically in the order of 2 to 100 microns thick. Lambda values are usually greater than 2.

Elastohydrodynamic lubrication (EHL)

Elastohydrodynamic Lubrication – or EHL – is a lubrication regime, a type of hydrodynamic lubrication, in which significant elastic deformation of the surfaces takes place and it considerably alters the shape and thickness of the lubricant film in the contact

From Figure 1 it is seen that wear decreases dramatically when we reach the hydrodynamic lubrication regime.

Tribofilms

A tribofilm refers to a thin layer that forms in a mechanical application due to interaction between lubricant molecules and the lubricated surfaces. Perhaps the most well-known and most studied tribofilms are those formed on ferrous metals in the presence of lubricants with the zinc dialkyldithiophosphate ZDDP additive. This successful lubricant additive in motor oils is still unbeaten as former of protective films on steel surfaces in combustion engines, and thus very essential in mixed lubrication and boundary lubrication regimes.

3. Wear in internal combustion engines

The wear problems seen so far can be categorized as follows:

- Mechanical wear
- Chemical wear
- Interaction with lubricants

In addition to this we also see that the fuel causes changes in emissions, which in turn has an influence of deterioration of exhaust after treatment systems.

Important reviews in recent time on the influence of alternative fuels on engine wear have been carried out by Nagy, [4-3] and Liu [2-2]. Many of their findings have been helpful in giving the rough overview in this report.

Common wear mechanisms in internal combustion engines can be summarized as:

- Abrasive
- Adhesive
- Surface fatigue
- Tribochemical reactions
- Erosion and cavitation

In abrasive wear mechanisms, the harder surface penetrate into the softer counterpart due to the normal load. Abrasive wear can also be caused by a third body, that has entered the space between the sliding surfaces.

Adhesive wear can occur due to mechanical interlocking or atomic forces binding the contacting surfaces together during the sliding motion. The main contributing factor to the tendency of a material to exhibit adhesive wear is its shear strength. In general, materials with lower surface hardness and shear strength tend to exhibit higher rates of adhesion.

Surface fatigue usually occurs under boundary and mixed lubrication, where higher shear forces act on the surfaces in contact.

In tribochemical wear, chemical reactions occurs between surfaces of the sliding pair and the interfacial medium (i.e. lubricant) or the environment. Chemical reactions are enabled or accelerated by mechanical stimuli. These chemical reaction consumes the contacting bodies and the interfacial medium, which leads to a loss of material.

Erosion is the process of material removal from a solid surface through a flowing gaseous or liquid medium. Cavitation can appear at the interfaces of systems where fast-moving pressure waves are able to travel in a liquid medium.

Material compatibility with current engine technology is important for the penetration of alternative fuels into the market. Fuel lubrication properties is a typical issue of concern when implementing alternative fuels. F. ex. bad lubrication properties of di-methyl ether (DME) may result in malfunction of fuel injection equipment. Thus, lubricity improvers and additives are required to prevent possible damage to the hardware. In these cases we observe mechanical wear as a result of the application.

In other cases the chemical composition of the new fuel will break down/corrode materials in the engine and cause chemical wear of the engine surfaces. The chemical properties can also be able to decompose the lubricant applied in the engine. In these cases we observe chemical wear as a result of the alternative fuel application. This is seen in many

applications with f. ex. bio-oils and alcohols. Typical precautions taken are surface coatings and changes in lubrication formulation.

Finally, an important type of wear is associated with the physical interaction/mixing of the fuel with the lubricant, which in turn deteriorates as a lubricating agent. This is seen f. ex. in cases with biodiesel applications where the fuel spray behaves differently from diesel sprays due to changes in physical fuel properties like viscosity.

Lubricants

A lubricant in principle consists of two parts: a base oil and some additives. The primary function of the base oil is to keep the machinery parts separated by a fluid layer at a minimum friction level. Furthermore the base oil should remove heat and wear particles. Finally, since the lubricant in order to fulfill the requirements of a modern lubricant should also contain some additives, it is required that the base oil is able to dissolve these additives.

Base oils

Traditionally the base oil was based on petroleum. As the demands on the lubricant has increased, the synthetic base oils has gained more and more market. The development of synthetic base oils started before The WW II in Germany and U.S.A. However, it was not until after the war that the synthetic lubricants gained a significant market share. Primarily this was catalyzed by a demand from military and aero-engineering purposes.

In recent time the concern about the environment has resulted in development of environmentally friendly lubricants based on vegetable oil. In this context several tests have been developed in order to characterize the biodegradability of lubricants. Vegetable oil based lubricants have superior characteristics in this respect as compared to synthetic lubricants, which again have superior characteristics compared to petroleum based lubricants.

An overview of the qualities of different oils are given in Table 1

From the table we see that mineral oils are very superior with respect to price, solubility of additives, hydrolytic stability and corrosion protection.

Polyalphaolefines are actually the perfect base lubricants, according to these tables. Except from the viewpoint of biodegradability, thermal stability (compared to ester oils) and lubricating properties (compared to rape seed oil), and of course the price cannot compare to mineral oil based lubricants.

Property	Min. oil	PAO	PEG	DAE	NPPE	RSO
Viscosity temperature behaviour (VI)	4	2	2	2	2	2
Low temperature behaviour (pour point)	5	1	3	1	2	3
Liquid range	4	2	3	2	2	3
Oxidation stability	4	2	3	2-3	2	5
Thermal stability	4	4	3	3	2	4
Evaporation loss, volatility	4	2	3	1	1	3
Fire resistance, flash temperature	5	5	4	4	4	5
Hydrolytic stability	1	1	3	4	4	5
Corrosion protection properties	1	1	3	4	4	1
Seal material compatibility	3	2	3	4	4	4
Paints and lacquer compatibility	1	1	4	4	4	4
Miscibility with mineral oil	-	1	5	2	2	1
Solubility of additives	1	2	4	2	2	3
Lubricating properties, load carrying capacity	3	3	2	2	2	1
Toxicity	3	1	3	3	3	1
Biodegradability	4	3-4	1-2	1-2	1-2	1
Price relation against mineral oil	-	3-5	6-10	4-10	4-10	2-3

Note: Min.oil: mineral oil; PAO: Polyalphaolefins; PEG: Polyalkylenglycols; DAE: Dicarboxylic acid esters; NPPE: Neopentyl polyesters; RSO: Rape seed oils

Grading 1: excellent; 2: very good; 3: good; 4: moderate; 5: poor

Table 1. Comparison and rating of different lubricant base oils [3-1].

Glycols generally don't have any excellent properties, except from biodegradability, and it is not suited for mixing with other lubricant fluids. Esters have a number of superior qualities like cold flow properties, thermal stability, volatility and biodegradability. Price is the major drawback as well as seals material compatibility and corrosion protection.

Rape seed oil is superior with respect to biodegradability, toxicity, lubricating properties and corrosion protection. The major drawbacks are oxidation stability, hydrolytic stability and seals material compatibility. Price of course cannot compete with mineral oil.

Additives

Some additives are particularly designed to act against friction and wear. These are “Friction modifiers”, working against friction and “Anti-wear additives”, working against wear .

Friction modifiers

Friction modifiers have the function of setting the appropriate friction coefficient characteristics for the lubricant. In most cases, the reduction of friction is the goal. Friction modifiers are compounds like: fatty acids, amines and amine phosphates.

Anti-wear additives

These additives stick to metal surfaces by polar forces and prevent contact between the moving bodies in the mixed-lubrication areas, thus preventing wear. Anti-wear additives are compounds like: phosphorus and Sulphur compounds, Zink dithiophosphates, olefins, fatty acid esters, Molybdenum disulphide and Graphite.

4. Natural oils, biodiesel and bio-oils

In this section, engine wear related topics are discussed for natural oils, biodiesel, paraffinic diesel and upgraded fast pyrolysis bio-oil.

- Finland contributed to AMF Task 62 with their experiences on upgraded pyrolysis bio-oil for marine transportation through the work of VTT in the national “BioFlex” project (website <https://www.bioflexfuel.fi/>). The BioFlex project has not yet addressed directly the wear issue, but is aware of the issues that could come up in future application of upgraded pyrolysis oil.
- University of Vaasa from Finland contributed with their experiences with a 20% blend of biodiesel from soy bean oil and 80% fossil diesel. These contributions are presented in the respective sections.
- DTU contributed in the part of the description of natural oils and biodiesel.

Many types of biobased fuels are suitable for diesel combustion in diesel engine. Table 4.1 presents selected pathways (feedstocks and processes) to produce bio-based fuels for diesel combustion. General features of pathways for natural oils, biodiesel, paraffinic diesel and fast pyrolysis bio-oil (FPBO) were reported in the AMF Task 34-1 [4-1].

Table 4-1. Feedstocks, processes and products relevant as biobased fuel for diesel engines.¹

Feedstock	Process	Product, end-use
Natural oils	No processing	<i>Natural oils</i> Food, energy
Natural oils	Esterification	<i>Biodiesel</i> (by-product glycerol) Transport fuels
Natural oils	Hydrotreatment	<i>“Paraffinic”, Hydrotreated vegetable oil (HVO)</i> Transport fuels
Biomass	Syngas → Fischer-Tropsch or Methanol-to-liquids processes	<i>“Paraffinic”, Synthetic fuels</i> Transport fuels, chemicals, fuel cells, power and heat
Biomass	Pyrolysis	<i>Fast pyrolysis bio-oils (FPBO)</i> Power and heat Feedstock for processing to engine use
FPBO	Hydroprocessing Feed to refinery	<i>Refined bio-oils</i> Potential transport fuel

¹ Covers selected biofuels suitable for diesel combustion. Note; e.g. alcohols via sugar platform or biomethane via anaerobic digestion are feasible for internal combustion engines.

Natural oils

Natural oils have cetane numbers in a range of 32-40, hence sufficient for a compression ignition diesel engine. However, their high viscosity prevents the use in modern high-speed engines, while natural oils may be used in large diesel engines. Viscosity of the rapeseed oil at 90 °C is close to that of diesel fuel, and some saturated fatty acids, such as those in palm oil and beef tallow, are solid at room temperature [4-2]. High viscosity of natural vegetable oils can result in various problems in conventional diesel engines, for example poor durability of the fuel injection system, improper spray formation, engine deposits and high exhaust emissions. High viscosity of natural oils aggravates the formation of a proper fuel spray leading to wetting of the combustion chamber and diluting the lubricant with fuel. This, in the long term, lowers the viscosity of the lubricant, and the oil film, which is supposed to protect metal surfaces, becomes too thin and excessive wear is the result.

Biodiesel

In order to produce improved fuel from natural oils, they are converted into "biodiesel" by transesterification, in which the triglyceride of the oils/fats with an alcohol forms fatty acid alkyl esters (biodiesel) and glycerin. Alcohol used in this process is typically methanol leading to fatty acid methyl esters (FAME). Table 4-2 shows that the esterification of vegetable oils decreases the viscosity of the fuel to a level closer to diesel, but still not to the same values. It is seen that the esterification process also improves the cetane number of the fuel. Storage stability is challenging for FAME biodiesel, since as a biological material it tends to be oxidized (biodegrade) with time. This could result in deposit formation and clogging of the fuel system depending in the case of insufficient quality control of FAME.

The fuel spray with biodiesel is still not as good as diesel: the fuel spray hits the cylinder wall for both biodiesel and a mixture of biodiesel and diesel, whereas this is not the case for diesel fuel. Beside the viscosity, the spray formation is also much dependent of the fuel surface tension. It is also mentioned that the higher evaporation temperature of fatty acid methyl esters implies a higher rate of oil dilution [4-3]. Therefore, it is recommended to increase the frequency of lubricant shift with biodiesel. Of course the engine design can be adapted to overcome some of the problems, however, increased cylinder wear is most likely a result of biodiesel application due to this phenomenon.

Biodiesel has in some cases shown better friction and wear performance than fossil diesel due to a lower coefficient of friction, C_f . This again is an effect of biodiesels' content of long-chain ester molecules, [4-4, 4-5]. Nevertheless, evidence are seen for cylinder wear and deposits as well as for fuel pump wear. However, some biodiesel fuels in the long term have shown incompatibility with metals and elastomers in IC engines. Biodiesels thus have shown corrosive and oxidation tendencies, [4-6]. Rapeseed methyl ester (RME) will for example be able to corrode Cu and Fe [4-7]. The corrosive nature of biodiesel is basically depending on temperature, water content, microbial growth and the type of feedstock applied, [4-8]. The dilution of lubricant with biodiesel is of concern because the lubrication properties are changed with the long term operation of the engine.

University of Vaasa presented Finnish experiences with application of so called B20 (~20% biodiesel from soy bean oil and 80% petrodiesel) [4-9]. Focus was on the lubricant, and the conclusion was that the lubricant could operate for more than 500 hours without notable deterioration of the lubricant. As expected from the literature the biodiesel was harsh on metals like Cu and Fe. However, also other metals were affected. It is a positive thing that the lubricant is not affected by fuel dilution.

“Paraffinic” HVO diesel fuels

In order to produce high-quality fuel from the natural oils and fats they can be hydrotreated to “paraffinic” “HVO” renewable diesel fuel. Furthermore, biomass can be converted to paraffinic “BTL” renewable diesel fuel by its gasification to syngas followed by the Fischer-Tropsch liquefaction process. From an engine perspective, this kind of paraffinic diesel fuels are the most suitable fuels for diesel engines, since their densities, viscosities and cetane numbers are at the same level as that for the fossil diesel fuel (Table 3). Paraffinic diesel components are of “premium grade” and they can be blended with diesel fuel in high concentrations or used as such depending on regional standards for fuel density and OEM specifications. Paraffinic components typically improve properties of diesel fuel leading to the reduced exhaust emissions and better engine performance [4-1].

Due to the low density of paraffinic fuels, lubricity additive is needed in the final blend to protect fuel injection equipment against excess wear. Paraffinic components are generally compatible with parts and materials, although low aromatic content may shrink elastomers if these have swollen when used with aromatic fuels. [4-1]. For paraffinic diesel fuel, similarly to petroleum diesel, additives at least for corrosion protection are needed. [4-1]. For all diesel fuels, some precipitation of paraffins may occur at temperatures below the cloud point of fuel.

Antistatic additive can be used in HVO to allow high pumping velocities, which otherwise would be limited due to the low electrical conductivity of HVO (comparable to that of sulfur-free diesel fuels). As regards using diesel-type in marine diesel engines is in principle straightforward, however, some challenges with residual marine diesel fuels may occur similarly as with all distillate-type diesel components (e.g., FAME, paraffins) due to the separation of asphaltenes from residual fuel. [4-10].

Table 4-2. Examples of fuel properties of natural rapeseed oil and its derived FAME biodiesel and paraffinic HVO.

	Rapeseed oil [4-11]	FAME (RME) [4-12]	HVO [4-13]
Kinematic viscosity at 40 °C (mm ² /s)	37	4.5	2.0-4.5
Cetane number	37-44	>50	>70
LHV (MJ/kg)	40	36	44

Refined fast pyrolysis bio-oil

The fast pyrolysis oils from waste or lignocellulosic feedstocks are challenging for internal combustion engines (ICEs), since these contain oxygen and acids, and their properties vary depending on the feedstock, production process, and degree of upgrading. Good quality bio-oils have been reported for the pyrolysis of recycled plastics and tyres, although e.g. polyvinyl chloride (PVC) is of concern regarding its chlorine content, and generally refining is needed to achieve suitable flash points, acid numbers, amongst other fuel properties. [4-14, 4-15, 4-16].

Finland contributed to AMF Task 62 with the VTT's "BioFlex" project (website <https://www.bioflexfuel.fi/>), with focus on the upgraded wood-based fast pyrolysis bio-oil. The results of the Bioflex project related on the quality and storage properties of upgraded fast pyrolysis bio-oil for marine transport stability are reported by Ohra-aho et al. [4-17] and referred here.

The unrefined fast pyrolysis bio-oil (FPBO) is not suitable for diesel engines [Ohra-aho_ [4-18, 4-19, 4-20, 4-21], although it is used in the industrial boilers with the combined Canadian-European FPBO production capacity exceeding 180 000 tonnes in 2021 [4-22]. Standards for bio-oil use in boilers are ASTM D7544 and EN 16900. [4-23, 4-24]. CEN WG148 created Technical Specification for FPBO and listed the needed steps before continuation in standardisation. These included need of upgrading. The FPBO is immiscible to diesel fuel, it has a high content of water (20–25 wt %) and oxygenates [4-25, 4-26]. Hence, upgrading of the FPBO is necessary when considering it as marine fuel to lower oxygen content, acidity, carbon residue and viscosity, and to elevate its heating value. In the refining of the FPBO, for example reactive carbonyls can be hydrogenated into less reactive compounds (e.g. alcohols) [4-27].

GoodFuels and BTG Biomass Technology Group BV in the Netherlands have announced of building a plant for producing upgraded pyrolysis fuel for shipping to utilise residues and wastes. [4-28]. So far the quality of the refined FPBO is not defined by fuel standards, which may lead to variable quality of components and their suitability as drop-in marine fuel. Even the analyses methods of the upgraded FPBO are under development, since methods developed for the other fuels may not be feasible. For example, oxidation of FAME forms volatile acids increasing the conductivity, while auto-oxidation is not expected for the refined FPBO. Improved methods are needed also for example for determination of the chlorine content and the acid number of the refined FPBO [4-29]. The development and validation of critical analytical methods could be done in co-operation with IEA Bioenergy Task 34, which has a long track of records on this type of work. (<https://task34.ieabioenergy.com/>).



Figure 4-1. Status of standardisation of the FPBO and upgraded FPBO.

In the Bioflex project, preliminary results recently reported by Ohra-aho et al. [4-17] were promising for a blend of upgraded FPBO (10%) and marine diesel oil use in a medium-speed engine, and hence higher blending ratios could be considered. Others have also reported of using hydrotreated FPBO as a marine fuel [4-30]. In the Bioflex project, the stabilized and

deoxygenated pyrolysis oil (SDPO, ~5 wt % oxygen) refined from wood-based FPBO was studied with analytical methods developed by VTT for the FPBO [4-24, 4-25, 4-31] and further developed for the SDPO, and by the medium-speed engine [4-17]. In the Bioflex project, the SDPO was blended with marine distillate fuel, since high temperatures needed to lower the viscosity of the residual fuels were deemed to be inappropriate for the SDPO (Figure 4-2). In-depth data was gained of the stability of the SDPO by using the new accelerated ageing test and long-term storage stability study over a one-year storage period.



Figure 4-2. Blends with DMB containing 10%, 30% and 50% of SDPO [4-17].

Appropriate long-term storage quality of the SDPO is important to ensure the expected engine performance and that the oxidation or decomposition products do not increase the engine wear. The fuel analyses of the SDPO batch showed that some properties still require consideration to meet the specifications for marine distillate fuel, such as density, viscosity, cetane number, flash point, acid number, water content, carbon residue, and ash content (Table 4-3). Analytical methods that still need to be developed for the SDPO include e.g. the oxidation stability, lubricity, chlorine and sulfur. Differences in two SDPO batches analysed in the Bioflex project were observed as reported by Ohra-aho et al. [4-17]; the other one leading to precipitates emphasising the standardisation needs to ensure the constant quality of SDPO production. Also, blending procedures need to be defined and standardised.

The Bioflex project did not study aspects such as decomposition products, corrosivity, and additives, which are important for engine wear considerations. Others have emphasized the concern of the corrosiveness of bio-oils [4-18, 4-19, 4-32, 4-33] and this needs to be verified also for the refined SDPO. An EU project LowCoBio (RISE, S coordinator, VTT, F, participant) will start late 2024/early 2025 targeting to create data on corrosivity of bio-oils including upgraded FPBO and catalytic FPBO. The project aims to provide guidance on adjusting the process conditions throughout the whole production process, from pretreatment to liquefaction and upgrading, so that product quality and yield remain high at the same time as the need for very expensive construction materials is avoided.

Table 4-3. Properties of one of two SDPO batches of the Bioflex project [4-17]

	SDPO example
Density at 15 °C, kg/dm ³	0.95
Viscosity at 40 °C, mm ² /s	17.5
Cetane number (IQT)	22
LHV, MJ/kg	38.8
Water, wt%	0.6
Oxygen, wt%	4.9
Acid number (TAN), mg KOH/g	0.08
Oxidation stability EN16091, min	50.5
Total sediment, wt%	<0.01
Carbon residue (MCR), wt%	0.95
Ash, wt%	0.006

To summarise, pyrolysis oil is associated with challenges in order to be applicable in diesel engines. Therefore, the BioFlex project focused on the upgrading the FPBO to a product that is suitable for this purpose, specifically to the SDPO (stabilized and hydro treated pyrolysis oil), which was tested in a medium-speed diesel engine. The quality and stability of SDPO seems to be quite good according to the BioFlex results. In wear context, engine durability and corrosion aspect still need to be studied. More specifically the following investigations are seen as important:

- Sufficient standardized upgrading process
- Sufficient standardized quality of the upgraded FPBO
- Adequate stability of upgraded FPBO and gathering more data on possible decomposition products during storage and how to avoid this sedimentation
- Methods for testing corrosivity of the upgraded FPBO

Natural oils, biodiesel and bio-oils - summary

Table 4-4 gives an overview of the findings on wear associated with the application of natural oils, biodiesel and bio-oils. The issues have been divided into three categories: mechanical wear issues, chemical wear issues and issues related to interaction with the lubricant.

Table 4-4. An overview of the issues that can affect engine wear with natural oils, biodiesel and bio-oils.

Mechanical issues	Chemical issues	Interaction with lubricant
Natural oils, biodiesel		
<p>Biodiesel may lower cylinder and fuel pump wear due to lower coefficient of friction and less soot formation</p> <p>Mechanical wear caused by dilution of lubricant with fuel</p>	<p>Tends to oxidize (biodegrade) with time – deposit formation and fuel clogging as a result</p> <p>Corrosive nature particularly for Cu and Fe, but also other metals and elastomers can be affected</p>	<p>Fuel spray inappropriate – fuel mixes with lubricant film on the cylinder liner as a result. Higher degree of cylinder wear is a consequence</p> <p>Higher evaporation temperature of biodiesel results in higher degree of lubricant dilution and cylinder wear.</p>
Paraffinic HVO, BTL		
<p>Lubricity and corrosion additives are needed similarly as for petroleum diesel</p>	<p>Paraffinic components are similarly compatible as petroleum diesel with parts and materials, although low aromatic content may shrink elastomers if these have swollen when used with aromatic fuels</p>	<p>Similar performance for paraffinic components as for petroleum diesel fuel.</p>
SDPO (upgraded FPBO)		
<p>Stability of the bio-oil, refined FPBO, studied in the Bioflex project was good, but this aspect needs to be studied further.</p>	<p>Corrosivity of the refined FPBO needs to be studied further.</p>	<p>Interaction of the refined FPBO with lubricant needs to be studied further.</p>

5. Alcohols

5.1. Ethanol

Ethanol wear issues are described in this chapter and in a more detailed report, which is a result of basically the work of IEA Advanced Materials for Transportation TCP, but in collaboration with The IEA Advanced Motor Fuels TCP [0-1].

Ethanol and engine wear

The octane number (ON) of ethanol is greater than that of gasoline, although its calorific value is lower, requiring a larger amount of fuel to produce the same engine power [5-1]. The role of bioethanol in the energy transition is unquestionable, not only because it is renewable but mostly because CO₂ emissions resulting from the use of ethanol as fuel are lower than those from gasoline even when a full life-cycle assessment is considered [5-2]. Mixtures of gasoline with ethanol produce lower concentrations of unregulated gaseous species such as sulfur dioxide (SO₂) and isocyanic acid (HNCO) as well as fewer harmful polycyclic aromatic hydrocarbons (PAHs) when compared with gasoline [5-3]. Moreover, the amount of particulate matter (PM) in the exhaust system is lower for fuels containing ethanol as compared with gasoline [5-3,5-4]. When the effects of the PM emitted from engines running on mixtures of gasoline and ethanol were evaluated in biological tests, they were shown to be less cytotoxic and to have lower levels of reactive oxygen species (ROS) and lower mutagenicity than for engines running on gasoline alone [5-3].

The literature addresses different aspects of the impact of ethanol on engine performance. A number of these publications are directed to the analysis of tribological outputs, i.e., friction and wear. Several tribological systems have been used in these studies, ranging from measurements in actual engines to laboratory tests; thus, care should be taken when exploring the results in light of the varying characteristics of each system. In addition, the materials in contact can vary in different publications, as can the percentage of ethanol in the fuel, from zero ethanol (E0) to 100% ethanol (E100). In fact, engines that use pure ethanol commonly use hydrated ethanol (with around 5% water) instead of anhydrous ethanol, as it does need to dissolve with the gasoline. Therefore, most publications that refer to E100 should instead refer to E95.

Tests conducted directly on spark ignition engines provide a comprehensive comparison of the tribological effect of different fuels. dos Santos Filho, et al. [5-5] ran a fired engine dynamometer with either Brazilian gasoline (E25) or with hydrated ethanol (E95), then characterized the engine components for comparison. By looking at the topography of the cylinder bores after testing, the authors concluded that localized wear at the bottom dead centre (BDC) was significantly more pronounced for E95 than E25, as shown in Figure 5.

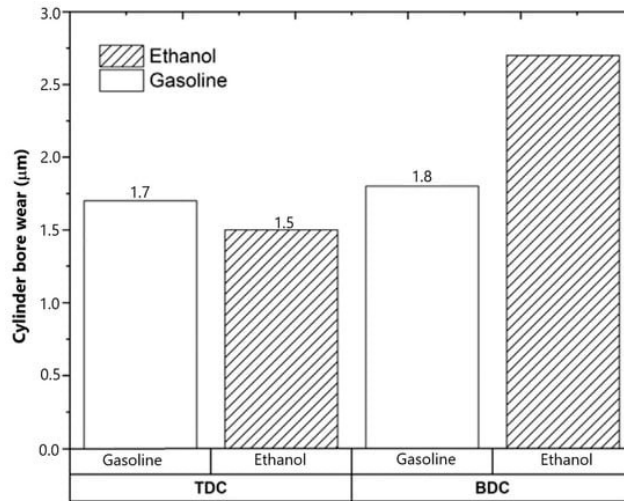


Figure 5. Effects of ethanol on wear of cylinder liners at the top dead centre (TDC) and bottom dead centre (BDC) as measured in engine tests [5-28].

Costa and Spikes [5-6] used MTM (Mini-Traction Machine) tests to analyse the impact of adding 5% of either anhydrous (AE) or hydrous ethanol (HE) on friction under different lubrication regimes. Under boundary lubrication conditions, ethanol in a fully formulated oil increased friction, probably by interaction with the lubricant additives, while it reduced friction in a base oil. Under mixed lubrication, ethanol increased friction for both the base oil and formulated lubricant, which was because the reduction in viscosity caused by ethanol led to thinner elastohydrodynamic (EHL) films, thereby increasing asperity contact. Under full film lubrication, ethanol reduced friction for both the base oil and formulated lubricant due to the viscosity reduction caused by the fuel dilution enabling the lubricant molecules to slide more easily in relation to each other.

Regarding the materials in tribological contact, different trends may be observed for the impact of ethanol on the lubrication of different materials. For example, Banerji, et al. [5-7] compared the friction and wear behaviour of an SAE 5W30 synthetic oil to its mixture with E85 (50% vol.) in unidirectional ball-on-disk tests. Ethanol dilution resulted in a significant decrease in friction coefficient for the contact of cast iron discs with DLC-coated AISI 52100 balls. However, the behaviour of diluted and undiluted oil was not significantly different when the cast iron disk was in contact with a cast iron counter-body. An opposite trend was observed in terms of wear, with ethanol dilution being responsible for significant differences in volumetric wear for the cast iron–cast iron contact and insignificant wear differences for the cast iron–DLC contact. Bandeira, et al. [5-8] studied the effect of ethanol contamination on coated materials in unidirectional sliding contacts. No significant differences were observed in terms of friction coefficients or wear rates when contaminated and non-contaminated oils were compared.

Influence of ethanol on lubricant properties

Compared to other fuels such as gasoline and diesel, bioethanol (anhydrous and hydrated) has a higher heat of vaporization [5-9] and higher boiling point [5-10]. These higher values enhance the possibility of unburned bioethanol condensation on the cylinder wall being dragged by the piston rings to the oil sump [5-11,5-12]. As a consequence, large amounts of

bioethanol may accumulate in the crankcase. In fact, amounts from 6% to 25% of diluted bioethanol and its combustion products have been found in the crankcase for both field [5-13,5-14] and engine tests [5-15,5-16,5-17]. This amount is higher for operating conditions that prevent proper heating of the lubricant, such as cold running conditions [5-18,5-19], short driving/testing cycles [5-13], start-stop technology [5-13], as well as higher concentrations of ethanol blended in the fuel. Higher concentrations of ethanol fuel in the oil sump impact the properties and performance of the lubricating oil in a different manner than gasoline, an issue that requires further investigation [5-9]. Furthermore, ethanol is more hydrophilic (dissolves easily in water) and hygroscopic (water-absorbing) compared to other fuels. Thus, the effect of water in the lubricant must be taken into account. The following section reviews the effects of ethanol on lubricant properties that are directly related to oil service life and performance.

During usage, it is common to observe oil acidification (increase in TAN) due to thermal oxidation and contamination with fuel and combustion byproducts; this is accompanied by a reduction in alkaline reserves (reduction in TBN), which are the compounds that neutralize acid products, as well as a slight reduction in viscosity due to thermal aging and fuel contamination [5-9,5-10]. This trend of viscosity and TBN reduction followed by an increase in TAN is accentuated by ethanol dilution [5-21,5-22]. At elevated temperatures, oxidation of fuel-oil mixture may generate peroxide in the presence of oxygen; this peroxide undergoes further reaction to form carboxylic acid, ketones, aldehydes, and alcohols, potentially resulting in a further increase in the acidity of the lubricant [5-23].

In real engine applications the lubricant ages due to thermal and fuel contamination. The acidification of the lubricant caused by thermal aging is accelerated by ethanol dilution due to its higher oxygen content. The role of temperature on lubricant properties has been scrutinized by a number of researchers. Most of the work has focused on comparing lubricant properties and the performance of fresh and thermally aged lubricants [5-24]. Essentially, these experiments consist of heating oil samples at different temperatures and times and then evaluating their friction and wear response through tribotests such as pin-on-disc and ball-on-disc. The overall observations indicate that aged lubricants present higher friction and wear values than corresponding fresh lubricant under mixed or boundary lubrication conditions. This is attributed to oil oxidation (increased TAN), which alters the dynamics of tribofilm formation. Tribofilms formed from thermally aged lubricants present a different molecular structure with a higher oxygen content [5-25,5-26]. A recent experimental methodology involved first contaminating the lubricant with different amounts of ethanol, then performing tribotests [5-27]. Analogously to the observation for thermally aged lubricants, the fuel-contaminated lubricants presented higher friction and wear in comparison to their fresh versions in steel-to-steel contact. The cause is similar in both cases, being due to tribofilm molecular structural changes; these are described in detail in [5-28]. However, such changes occurred even without oil oxidation, and the tribofilms formed in the presence of ethanol did not present the same structure as tribofilms formed from thermally aged lubricants [5-26]. Thus, tribofilm formation and lubricant performance are affected by tribofilm oxidation and lubricant oxidation, leading to higher friction losses and wear [5-24,5-29]. Such acidification of the lubricant increases oxidative and corrosive wear, as observed by the presence of black oxides (magnetite), pits, and mass loss [5-9].

Viscosity reduction due to fuel dilution has been observed by several researchers in both field [5-21,5-26] and lab tests [5-30,5-31,5-32], which is mostly due to the much lower viscosity of ethanol in comparison to usual engine lubricants. On the one hand, engine tests comparing gasoline and gasoline with different concentrations of ethanol showed that

viscosity reduction over time depends much more on the lubricant type than the fuel type, as both gasoline and ethanol have much lower viscosity than engine lubricants [5-21]. On the other hand, Costa and Spikes [5-30] found larger viscosity reductions for anhydrous than hydrated ethanol diluted in the lubricant. The authors hypothesized that the true solubility of the ethanol in the lubricant is lower for hydrated ethanol, resulting in some of the ethanol forming a microemulsion with water, which has little influence on lubricant viscosity. Modern engines lubricated with synthetic oils presented lower viscosity reduction than simpler mineral oils. After field tests of 3000 km performed with four motorcycles fuelled with gasoline and a mixture of gasoline and ethanol, the viscosity decreased by about 20% and 45% for synthetic and mineral-based oils, respectively, regardless of the fuel used [5-26]. Oil oxidation did not take place after 3000 km regardless of the tested lubricant and fuel. However, it should be pointed out that tribofilm formation is compromised in the presence of ethanol, even in the absence of oxidation.

It is important to point out that viscosity reduction might bring benefits in terms of friction reduction [5-33] for components operating under full film lubricating conditions, as lower viscosity reduces shear losses in the lubricant [5-30]. However, as further detailed in [5-29] the reduced viscosity makes the contact conditions more severe for mixed and boundary lubricating conditions, which may lead to higher friction values and wear [5-19,5-24,5-26,5-30,5-32].

Soot emissions from alcohol-fuelled engines are lower relative to other fuels; hence, reduced soot loading enhances the lubricating oil life [5-34]. On the other hand, ethanol is known to cause higher lubricant oxidation than gasoline. Ethanol is a polar solvent that can break down the additives in engine oil, leading to increased oxidation and degradation of the lubricant. In comparison, gasoline has lower solvency and is less likely to cause lubricant oxidation and additive degradation under the same levels of contamination [5-35].

In the case of ethanol–lubricant mixtures giving rise to acetic acid formation during operation [5-36], there is likely to be intensified oxidation and significant resulting sludge formation. This was observed by Besser, Schneidhofer, Dörr, Novotny-Farkas and Allmaier [5-35], who verified that the addition of acetic acid accelerates the ageing process by increasing oxidation, neutralization number, and sludge formation as well as slightly reducing TBN in comparison to neat lubricant or lubricant mixed with ethanol. However, in the absence of acetic acid ethanol is less likely to form sludge than gasoline.

Figure 6 attempts to summarize the effects of ethanol on lubricant properties and how it affects deposition formation throughout the lubricant lifetime. The use of lubricant decreases TBN and increase TAN, with both effects becoming more severe in the presence of ethanol contaminating the lubricant. Viscosity does not change much during lubricant use (only a slight decreasing tendency) up to a certain point that defines the lubricant lifetime. Within this period, ethanol reduces the lubricant viscosity. Afterwards, intense deposit formation should lead to a significant increase in lubricant viscosity. The onset of intense deposit formation occurs earlier for lubricants contaminated with ethanol, meaning that ethanol reduces the operation limit, thereby shortening the lubricant lifetime. Afterwards, the more intense deposit formation in the presence of ethanol should increase lubricant viscosity compared with neat lubricant.

Engine oil Degradation

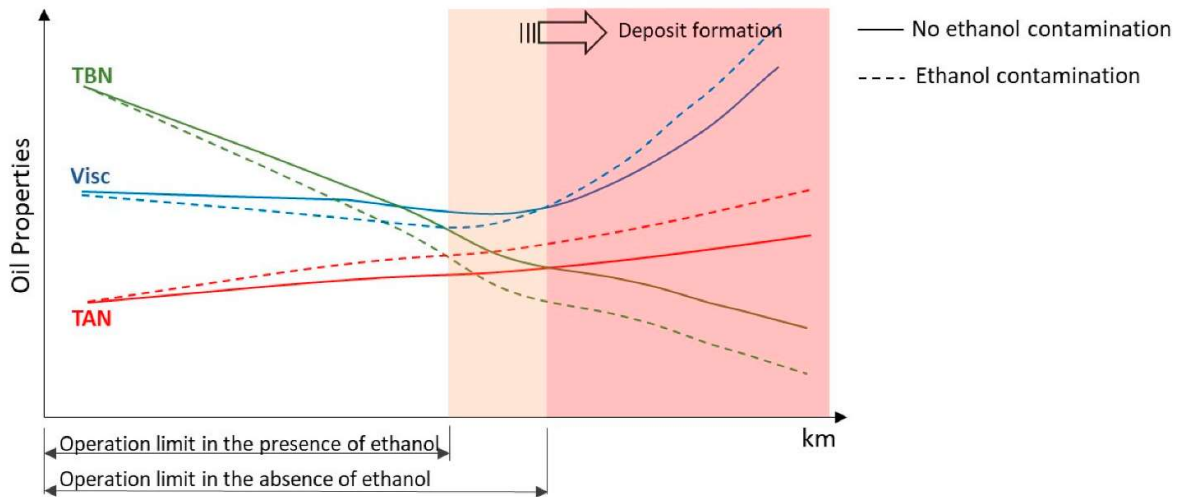


Figure 6. Effects of ethanol contamination on lubricant properties and deposit formation throughout the lubricant lifetime.

Lenauer, et al. [5-37] conducted an artificial engine oil alteration process with addition of ethanol combustion products to the oil, which was later used in reciprocating sliding laboratory tests. Two fully formulated oils were considered (SAE 15W40 and 5W30). The ethanol combustion products were acetaldehyde and acetic acid. The results indicated that the contaminants resulted in significant changes in the friction behavior of the 15W40 oil, but did not for 5W30. Both contaminants provided similar results in terms of wear for the two oils, increasing wear rates during running-in and lowering wear rates during the steady-state regime.

The tribological impact of ethanol is not restricted to conditions where ethanol contaminates the lubricant oil. High-frequency reciprocating rig (HFRR) tests were conducted to analyze the impact of water contamination on ethanol lubricity [5-38]. The results showed that water did not result in significant changes in coefficient of friction, while the aspect of the wear scar was modified, showing a trend of decreasing wear scar diameter with the increase in water fraction. HFRR tests have been selected to study the impact of ethanol on the lubricity of various formulations of gasoline as well. The results indicate that ethanol may enhance the lubricity of gasoline [5-39], and may form protective carbon-rich tribofilms on certain metallic surfaces [5-40].

Zinc dialkyldithiophosphate (ZDDP) is a very important antiwear additive in engine lubricants. In fact, the performance of automotive lubricants strongly relies on the presence of tribofilms formed from ZDDP to protect engine parts against wear [5-41]. This tribofilm has a very complex structure which may be influenced by the presence of ethanol in the lubricant. Experimental evidence has indicated that the formation of ZDDP tribofilms is induced by shear stresses produced by contact [5-42], involving an initial reaction of sulfur and phosphorus with metallic surfaces that forms sulphides and phosphates. The zinc present in ZDDP forms zinc sulphide at the interface with the metallic surface (which contains iron sulphide), whereas the continuous decomposition of ZDDP forms additional phosphates that react with zinc phosphate, leading to long-chain zinc polyphosphates. Near the tribofilm surface, long-chain zinc polyphosphates prevail [5-43]. According to Martin [5-

44], the sulphides near the metallic interface can react with iron that is continuously exposed when the surface is rubbed, preventing its being attacked by oxygen and thereby protecting the surface against severe wear by iron oxide debris.

However, when the lubricant is contaminated with ethanol this tribofilm may be substantially altered. When adding small amounts of ethanol fuel to a formulated lubricant in ball-on-disk tests using a mini-traction machine (MTM), Costa and Spikes [5-30] found that although ethanol slightly reduced friction under conditions where an elastohydrodynamic film was formed, due to a small reduction in lubricant viscosity it interfered with the tribofilm formed in the boundary lubrication region, increasing the coefficient of friction. These results prompted an investigation of the impacts of ethanol contamination (both anhydrous and hydrated) of lubricants containing ZDDP on the growth and stability of anti-wear tribofilms using the MTM-SLIM technique [5-32]. The results showed that ethanol significantly retarded the growth of ZDDP tribofilm. Moreover, the final tribofilm was particularly thin and irregular.

Ethanol - Summary

Mechanical issues	Chemical issues	Interaction with lubricant
Lower viscosity of the lubricant can be an advantage during HD and EHD lubrication, but makes the lubrication conditions worse during mixed and boundary lubrication.	Ethanol reacts with the lubricant, increasing the acidity of the lubricant (TAN). This influences tribofilm formation and causes increased wear.	Ethanol has a higher boiling point and heat of vaporization –ethanol therefore has a higher condensation rate on the cylinder liner, and fuel mixes with lubricant as a result. Lower viscosity and higher degree of cylinder wear is a consequence.
Increased wear scar diameter with higher water content of the lubricant	Ethanol is a polar solvent that can break down additives in the lubricant. Effects are seen on tribofilm formation caused by the ZDDP decomposition	Ethanol is more hydrophilic and hygroscopic compared to other fuels. The influence of water in lubricant must therefore be taken into account.
Fuel line clogging due to ethanol stripping of fuel system deposits	Degradation of some rubber and plastic materials	Water in the lubricant is seen to affect tribofilm formation
Fuel pump experiments with E22 showed abrasive wear (no water in fuel, so no corrosive wear?)	Degradation of metals due to the acidic or galvanic nature of ethanol. Water contamination of ethanol increase this type of corrosion significantly	

	Fuel pump experiments with E100 showed corrosive wear (caused by the water content of the fuel?)	
--	--	--

Table 5. Summary of ethanol issues that can affect engine wear.

5.2. Methanol

In China methanol has been applied in engines for a long time, and the Chinese experiences with wear in connection with methanol applications are reported in a separate report as a part of this study [0-3]. In the report wear on different parts of the engine has been investigated separately. In Table 6 a summary of the findings are listed.

Methanol summary:

<p>Fuel supply system:</p>	<p>-Seals should be made of modified nitrile rubber (to avoid swelling).</p> <p>-Epoxy resin sealing adhesive materials should be avoided</p> <p>Fuel pump:</p> <p>-Methanol is corrosive to metals such as tin, lead aluminum copper, magnesium. Plastic coatings on the stator and stainless steel rotor wrapping avoids the problems.</p> <p>Fuel injectors:</p> <p>-Same issues as for “fuel pump”. Stainless steel material and surface coatings needed</p>
<p>Engine Valve Train:</p>	<p>-Especially problems with exhaust valve erosion is seen. This is caused by extremely high mechanical and thermal loads. Alloy materials with better wear and corrosion resistance are needed.</p> <p>-Valve seat rings also needs special attention (choice of materials) to improve wear and corrosion resistance.</p>
<p>Cylinder liners and pistons:</p>	<p>-Methanol combustion products have a significantly negative impact on anti-wear performance of the engine lubricant. Formic acid has the greatest impact in this context.</p> <p>-Methanol containing water causes more wear than anhydrous methanol, and wear increases when the cooling water temperature is low.</p>

	<ul style="list-style-type: none"> -Methanol, lubricant and water forms an emulsion at low temperatures, causing the lubricant to fail. -Lubricants with improved alkali value and antioxidant properties are required for engines operating on methanol. -Cylinder liners of high chromium cast iron can significantly improve engine wear resistance -Steel pistons can meet the operating conditions of methanol. -Special coated piston rings improves the engine operation.
<p>Other issues:</p>	<ul style="list-style-type: none"> -Blocking of lubricant filter is seen. -Spark plugs undergoing pitting and ablation is seen.

Table 6. Summary of Chinese investigation of methanol issues that can affect engine wear in different parts of the engine.

6. Fuels with high hydrogen content

Conventional fuels like diesel and gasoline have a molar hydrogen/carbon (H/C) ratio in the neighborhood of 2. However, many of the alternative fuels have a high hydrogen content, and therefore a higher H/C ratio, which can be a disadvantage in relation to engine wear. The below mentioned fuels are relevant examples of such fuels. The wear issues for these fuels are described in general in this chapter, and the special issues in relation to the high H/C content are described in a separate report [0-4] published in connection with Task 62.

6.1. Methanol

The general methanol wear issues are described in chapter 5b and in the detailed task report [0-3] and summarized in chapter 5.2.

6.2. Ammonia

Ammonia has not been applied in combustion engines for longer time. At present there are no commercial ammonia engines on the market. Therefore, there are not many experiences with the influence of ammonia on engine wear.

Older engine studies [6-1] showed no unusual detrimental effects on bearing metals, except copper. Newer studies [6-2,6-3,6-4] have shown concern about different industrial materials, however, this mainly arise from knowledge about ammonia being more corrosive than traditional diesel and gasoline. [6-5] concluded that copper alloys are not recommended for an ammonia environment, but steel showed good resistance to ammonia derived corrosion. On top of that, ammonia in some cases can actually have a positive effect on surface hardness by the formation of nitride [6-6]. However, [6-7] did find that dedicated materials are needed for fuel injectors and fuel lines due to ammonia derived corrosion effects. [6-8] also reported indications of severe wear in traditional diesel nozzles operating with ammonia.

[6-1] investigated the effects of ammonia application on the lubricant properties, and only minor effects were discovered. A recent study [6-9] used an admixture of various contaminations to air, such as ammonia and its partial combustion product nitrogen dioxide, and investigated their respective impacts on chemical oil degradation. Their conclusions where that oxidation was low when utilizing stoichiometric NH₃ as a reaction gas mixture compared to air. The presence of aminic degradation products was indicated in the oils altered with trace and stoichiometric NH₃ reaction gas. An increase in kinematic viscosity can be attributed to the aminic species. Corrosiveness against copper was shown when stoichiometric NH₃ was used as a reaction gas. Both trace and stoichiometric NH₃ concentration impacted the deposit control performance severely compared to air or NO₂. Lubricants altered with stoichiometric NH₃ reached the lowest failure load (EP performance) amongst the samples.

So called stress corrosion crack has been reported for different materials in ammonia storage tanks. Cracking of C-Mn steel and copper alloys have been reported [6-10,6-11,6-12].

[6-9] concludes that it is clear that the impact of ammonia as a fuel towards the lubrication system must be investigated to enable the provision of long-life, reliable lubricants for use in such powertrain systems. Additionally, the detailed analysis of lubrication performance, e.g., in a piston ring–cylinder liner contact, has to be thoroughly assessed in the future if ammonia is going to be used as a fuel.

6.3. Hydrogen

Several studies have shown that surfaces exhibit higher wear rates in a hydrogen atmosphere compared to an air atmosphere [2-2]. Hydrogen exhibits a more corrosive environment in combustion engines than conventional fuels. This should lead to problems with engine components. However, even though several compounds were affected, [6-13] found that only minor issues were detected when comparing gasoline and hydrogen application in field test combustion engines. In laboratory tests they discovered fuel injector failure, since hydrogen is not able to lubricate sufficiently the moving parts inside the injectors. Embrittlement is often seen as a result of hydrogen application. Particularly valves and valve seats are seen to be affected [2-2]. [6-14] in addition found scuffing and severe sludge and varnish formation in the crank case and on the cylinder liner in a test engine.

According to [2-2] the excessive combustion of water may lead to emulsification and thus compromise the lubricating oil capacity. [6-15] have detected that the properties of lubricating oil applied in a hydrogen-fueled V8 SI engine have significantly changed with a severe decrease of the lubricity, compared with that of the unused oil. The concentration of additives in the used oil was remarkably decreased, and the esters almost disappeared entirely. [6-16] observed oil contamination in an engine fueled with 18% hydrogen blended CNG. Compared with pure CNG, the hydrogen blends can lower the viscosity of lubricating oil together with a decreased oil film thickness in the cylinder liner-piston rings tribo-system. It is also detected that the TBN of the lubricating oil was lower in the engine fueled with 18% hydrogen-CNG, and the formation of acidic compounds accelerated corrosive wear. Furthermore, the wear debris accumulates in used oil, particularly the Fe and Cu facilitates the stripping of polar additives in the oil.

The absence of oxygen in the hydrogen environment may prevent formation of oxides which in turn is supposed to protect surfaces against wear. Hydrogen also facilitates wear by formation of hydrides or hydroxide/oxide layers [6-17,6-18].

Surface embrittlement caused by hydrogen furthermore will enhance formation of small particles which in the end could cause abrasive wear at sliding surfaces [2-2].

Tribo-corrosion is another form of material degradation in humid or aqueous environments through the combined wear-corrosion process [6-19]. The friction process in a hydrogen environment is often accompanied by the water in lubricant oil and/or water vapor in the air, which creates a condition favorable for tribo-corrosion. The presence of water may cause hydrogen reduction, leading to the formation of hydrogen peroxide and the hydrogen free-radical at the plastically deformed surface of worn parts [6-20]. It has been suggested that hydrogen in atomic form is more prone to be absorbed, whereas hydrogen peroxide is a strong oxidant and reacts violently with certain metals.

6.4. DME

Combustion of DME is associated with very low soot formation and lubricant contamination with soot is therefore not an issue. Low viscosity causes leakage problems within the fuel supply system. To prevent this issue it is necessary to choose appropriate sealing materials in the fuel-injection systems.

Low lubricity leads to the surface wear problems of moving parts within the fuel-injection system. The problem can be solved by the adaptation of the materials of the bearing surfaces and plunger/barrel interfaces to the low lubricity of DME. However, this solution

technically is very complex and expensive. Additives that are commonly used to improve lubricity of some diesel fuel grades, and also new additives, have been tested for DME. However, dosing levels of additives have been high. [6-21,6-22].

Dimethyl ether is non-corrosive, but is an excellent solvent, which can dissolve a number of elastomers most commonly used in the diesel engines as well as other plastic components [6-23]. To prevent seals quality deterioration after prolonged exposure of DME, it is necessary to carefully select appropriate sealing materials (such as polytetrafluoroethylene (PTFE)).

The high vapor pressure of DME means that cavitation can take place, which in turn impedes stable fuel injection operation. To avoid cavitation the fuel supply pressure (the feed pressure from the storage tank to the fuel pump) must be between 1.2–3 MPa [6-23,6-24].

Special fuel injection systems have been studied for DME, such as wear-self compensation nozzle and independent lubrication nozzle [6-25,6-26]. In early 2000's, DME was not compatible with the most conventional gasket and seal materials, but promising elastomers have been found [6-27].

6.5. The influence of fuel H/C ratio on engine wear

Fuels with higher H/C ratios produce more water in the exhaust. As mentioned earlier this is suspected to increase wear in engines. Therefore, a special experimental investigation was carried out in order to quantify the effect of the water exhaust concentration. This investigation is reported in a separate report of Task 62 [0-4].

Fuels with high hydrogen content - summary

Mechanical issues	Chemical issues	Interaction with lubricant
<p>Ammonia:</p> <ul style="list-style-type: none"> -Stress corrosion cracks reported in ammonia storage tanks. -Excessive wear is expected due to water condensation on the cylinder liner 	<p>Ammonia:</p> <ul style="list-style-type: none"> -Corrosive effects on copper alloys, but probably also on other materials (not much experience so far). -More experience is needed with ammonia application. 	<p>Ammonia:</p> <ul style="list-style-type: none"> -Only minor effects have been reported. -An increase in lubricant kinematic viscosity due to aminic species has been reported. -More experience is needed with ammonia application.
<p>Hydrogen:</p> <ul style="list-style-type: none"> -Surface embrittlement reported. -Embrittlement causes formation of small particles that can lead to abrasive wear. 	<p>Hydrogen:</p> <ul style="list-style-type: none"> -Absence of oxygen prevents formation of protective oxides. -Excessive water concentrations seen to cause tribo-corrosion. 	<p>Hydrogen:</p> <ul style="list-style-type: none"> -Emulsification of lubricant seen. -Hydrogen application seen to decrease lubricant additive concentration and esters almost disappeared. -Lubricant TBN affected by hydrogen application.

<p>-Fuel injector failure seen due to hydrogens bad lubricity effect.</p> <p>-Excessive wear is expected due to water condensation on the cylinder liner</p>		<p>-Wear debris seen to cause stripping of polar additives in the lubricant.</p>
<p>DME:</p> <p>-The low lubricity of DME causes surface wear problems of moving parts in the fuel injection system.</p>	<p>DME:</p> <p>-DME is an excellent solvent, and dissolves many engine materials. Special care needs to be taken when choosing engine materials.</p>	<p>DME:</p> <p>-DME lubricity is very low</p>
<p>Methanol:</p> <p>-See chapter 5.2</p> <p>-Excessive wear is expected due to water condensation on the cylinder liner</p>	<p>Methanol:</p> <p>-See chapter 5.2</p>	<p>Methanol:</p> <p>-See chapter 5.2</p>

Table 7. Summary of wear issues with ammonia, hydrogen, DME and methanol.

7. Conclusions

A review of wear associated with application of the most relevant alternative fuels in combustion engines has been carried out.

Important players on the international scene have contributed with their experiences of application of fuels. China has been an important participant with respect to methanol applications, Brazil has been important with their extensive knowledge of ethanol application, and research institutions from Denmark, Finland and Germany have covered a broader area of biofuels and fuels with high content of hydrogen (ammonia alcohols, DME and pure hydrogen).

The wear problems seen can be divided into 3 major categories: mechanical issues, chemical issues and interaction with the lubricant. Major bullet points summarizing the findings in these categories for each fuel are listed in the Table 4 (bio-oils), Table 5 (ethanol), Table 6 (methanol) and Table 7 (ammonia, DME and hydrogen).

Precautions should be taken to avoid engine wear problems associated with application of alternative fuels. This means that careful choice of engine materials and lubricants must be done.

For biofuels suitable for diesel combustion, the major problems are associated with dilution of lubricant with fuel, the fuel tends to biodegrade and corrosive nature is seen towards some materials.

For ethanol, wear conditions are worsened due to lowering lubricant viscosity and due to water content in the lubricant. Ethanol, furthermore, reacts with the lubricant. This increases the acidity of the lubricant and the break down of some lubricant additives. On top of this, increased water content of ethanol, which is often seen, increases engine corrosion.

For methanol, the same issues as for ethanol with water is seen. Chinese experiences concludes on more specific material issues which are summarized in Table 6. Furthermore, formation of formic acid has a negative impact on anti-wear performance. Methanol, lubricant and water forms an emulsion at low temperatures which can cause lubricant to fail. Lubricants needs improved alkali values and antioxidant properties for the engines to work properly. Finally, spark plugs undergoing pitting and ablation is seen.

Hydrogen is reported to cause surface embrittlement, fuel injector failure (due to bad lubricity) and prevention of formation of surface protective oxides. Furthermore, hydrogen is seen to decrease lubricant additive content in many different ways, and it can cause emulsification of the lubricant. Finally excessive wear is caused by water condensation on the cylinder liner.

Ammonia is a relatively new fuel for combustion engine applications. Therefore, much more experience is needed to describe the fuel impact on wear completely. However, corrosion effects on copper alloys are reported, and it is expected that this is also the case for other materials. Increase in lubricant viscosity has been reported and high water content in the exhaust is expected to cause excessive wear due to water condensation on the cylinder liner.

DME is a relatively well investigated alternative fuel since this was seen as a highly potential fuel to substitute diesel in the early 2000's. The problems with DME is that it is an excellent solvent which can cause damage to most materials. However, materials resistant to DME have been identified due to huge interest in applying DME in the early 2000's. DME's low lubricity has caused surface wear in the fuel injection system. Additives have been developed to mitigate this problem.

8. References

- [0-1] Costa H et. Al. "Review – Tribological Challenges in Ethanol – Fueled Engines". **IEA Advanced Materials for Transportation TCP**, July 2024.
- [0-2] Schramm J et. I. "Wear associated with application of methanol in combustion engines – Main report" **IEA Advanced Motor Fuels TCP – Task 62**, September 2024.
- [0-3] Wei A et. Al. "Wear associated with application of methanol in combustion engines – Chinese experiences" **IEA Advanced Motor Fuels TCP – Task 62**, September 2024.
- [0-4] Christensen R et. Al. "The influence of fuel H/C ratio on engine wear – An experimental investigation". **IEA Advanced Motor Fuels TCP – Task 62**, September 2024.
- [2-1] Bartz WJ "Handbuch der Tribologie und Smierungstechnik, Band 8 - Tribological Relationship as Basis for the Solution of Friction and Wear Problems" **Expertverlag**, 1994.
- [2-2] Liu Z et. Al. "A comprehensive review on the material performance affected by gaseous alternative fuels in internal combustion engines". **Engineering Failure Analysis**, 139, 106507, Elsevier Ltd. 2022.
- [3-1] van Walwijk M et.al. "Biodegradable Lubricants". **IEA Advanced Motor Fuels Agreement – Annex XVI**, December 1999.
- [4-1] **AMF Fuel Info**: https://www.iea-amf.org/content/fuel_information/fuel_info_home. (accessed 2024-10-13)
- [4-2] R. McGill, P Aakko-Saksa and N-O Nylund. **AMF Task 34-1**. Biomass-Derived Diesel Fuels. Task 1: Analysis of Biodiesel Options. 2009. (https://iea-amf.org/app/webroot/files/file/Annex%20Reports/AMF_Annex_34-1.pdf).
- [4-3] Nagy AL et al. "A Review on the Effect of Alternative Fuels on the Friction and Wear of Internal Combustion Engines". In "Vehicle and Automotive Engineering 2, edited by Károly Jármái Betti Bolló. **Proceedings of the 2nd VAE2018, Miskolc, Hungary**". Springer 2018.
- [4-4] Rahman, M et. al. "Study on the tribological characteristics of australian native first generation and second generation biodiesel fuel". **Energies** 10, 55, 2017. old[9]
- [4-5] Xu, Y et. al. "Friction and wear behaviors of catalytic methylesterified bio-oil". **Tribol. Int.** 71, 168–174, 2014. Old [10]
- [4-6] Haseeb, ASMA et. al. "Compatibility of automotive materials in biodiesel: a review". **Fuel** 90, 922–931, 2011. old [11]
- [4-7] Hu, E et. al. "Corrosion behaviors of metals in biodiesel from rapeseed oil and methanol". **Renew. Energy**. 37, 371–378, 2012. old [12]
- [4-8] Singh, B et. al. "A critical review on corrosion of compression ignition (CI) engine parts by biodiesel and biodiesel blends and its inhibition". **Renew. Sustain. Energy Rev.** 16, 3401–3408, 2012. old [13]
- [4-9] Sirviö, K., Niemi, S., Katila, T., Ovaska, T., Nilsson, O., Hiltunen, E. "B20 fuel effects on engine lubricating oil properties". **CIMAC Congress**, Helsinki June 6-10, 2016.

- [4-10] Aakko-Saksa, P., Lehtoranta, K., Kuittinen, N., Järvinen, A., Jalkanen, J-P., Johnson, K., Jung, H., Ntziachristos, L., Gagné, S., Takahashi, C., Karjalainen, P., Rönkkö, T., Timonen, H. Reduction in greenhouse gas and other emissions from ship engines: Current trends and future options, **Progress in Energy and Combustion Science**, Volume 94, 2023, 101055, doi.org/10.1016/j.pecs.2022.101055.
- [4-11] Barnwal, B.K. and Sharma, M.P. Prospects of biodiesel production from vegetable oils in India. **Renewable and Sustainable Energy Reviews**, 9, 2005, 363-378.
- [4-12] Murtonen, T. and Aakko-Saksa, P. Alternative fuels with heavy-duty engines and vehicles – VTT contribution. 2009, **VTT Working Papers 128**.
- [4-13] Mikkonen, S., Hartikka, T., Kuronen, M. and Saikkonen, P. (2012) HVO, hydrotreated vegetable oil – A premium renewable biofuel for diesel engines. 2012, <http://www.nesteoil.com/default.asp?path=1,41,11991,12243,12335>
- [4-14] Y.H. Teoh, H. Yaqoob, H.G. How, T.D. Le, H.T. Nguyen. Comparative assessment of performance, emissions and combustion characteristics of tire pyrolysis oil-diesel and biodiesel-diesel blends in a common-rail direct injection engine, **Fuel**, 313 (2022), 10.1016/j.fuel.2021.123058
- [4-15] W.K. Hussam, M.N. Nabi, M.W. Chowdhury, M.E. Hoque, Rashid A Bin, M.T Islam. Fuel property improvement and exhaust emission reduction, including noise emissions, using an oxygenated additive to waste plastic oil in a diesel engine, **Biofuels, Bioprod Biorefining**, 15 (2021), pp. 1650-1674, 10.1002/bbb.2262
- [4-16] F.M. Hossain, M.N. Nabi, T.J. Rainey, T. Bodisco, T. Bayley, D. Randall, et al. Novel biofuels derived from waste tyres and their effects on reducing oxides of nitrogen and particulate matter emissions. **J Clean Prod**, 242 (2020), Article 118463, 10.1016/j.jclepro.2019.118463
- [4-17] Ohra-aho T., Oasmaa, A., Koponen, P., Nyyssönen, S., Tuominen, V. and Aakko-Saksa, P. Quality and Storage Properties of Upgraded Fast Pyrolysis Bio-Oil for Marine Transport. **Energy & Fuels** 2024, 38, 20, 19566-19583.
- [4-18] Oasmaa, A.; Lehto, J.; Solantausta, Y.; Kallio, S. Historical Review on VTT Fast Pyrolysis Bio-Oil Production and Upgrading. **Energy Fuels** 2021, 35 (7), 5683–5695.
- [4-19] Solantausta, Y.; Nylund, N.-O.; Westerholm, M.; Koljonen, T.; Oasmaa, A. Wood-Pyrolysis Oil as Fuel in a Diesel-Power Plant. **Bioresour. Technol.** 1993, 46 (1–2), 177–188.
- [4-20] Jay, D. C.; Rantanen, O.; Sipila, K.; Nylund, N.-O. Wood Pyrolysis Oil for Diesel Engines. In Proceedings of the **1995 Fall Technical Conference**; Milwaukee, 1995.
- [4-21] Chiaramonti, D.; Oasmaa, A.; Solantausta, Y. Power Generation Using Fast Pyrolysis Liquids from Biomass. **Renewable and Sustainable Energy Reviews** 2007, 11 (6), 1056–1086.

- [4-22] Oasmaa, A., Ohra-aho, T., Venderbosch, R. Bio-Liquids for Co-Refining – Determination of Quality **ACS Fall 2020 Virtual Meeting & Exposition** August 17-20, 2020.
- [4-23] Oasmaa, A., van de Beld, B., Saari, P., Elliott, D. C. & Solantausta, Y. Norms, standards, and legislation for fast pyrolysis bio-oils from lignocellulosic biomass, 2015, **Energy & Fuels**. 29, 4, p. 2471-2484.
- [4-24] Lehto, J., Oasmaa, A., Solantausta, Y., Kytö, M. & Chiaramonti, D. Fuel oil quality and combustion of fast pyrolysis bio-oils, 2013, Espoo: VTT Technical Research Centre of Finland. 79 p. **VTT Technology; No. 87**.
- [4-25] Oasmaa, A.; Peacocke, C. Properties and Fuel Use of Biomass-Derived Fast Pyrolysis Liquids. **A Guide**, Vol. 731, 2010.
- [4-26] Oasmaa, A.; Sundqvist, T.; Kuoppala, E.; Garcia-Perez, M.; Solantausta, Y.; Lindfors, C.; Paasikallio, V. Controlling the Phase Stability of Biomass Fast Pyrolysis Bio-Oils. **Energy Fuels** 2015, 29 (7), 4373–4381.
- [4-27] Buechele, M.; Lutz, H.; Knaus, F.; Reichhold, A.; Venderbosch, R.; Vollnhofer, W. Co-Feeding of Vacuum Gas Oil and Pinewood-Derived Hydrogenated Pyrolysis Oils in a Fluid Catalytic Cracking Pilot Plant to Generate Olefins and Gasoline. **Open Research Europe** 2021, 1, 143.
- [4-28] Vries R De, The role of renewable marine fuels, **Sustainable Magazine** (2020).
- [4-29] Christensen, E.; Ferrelln, J.; Olarte, M. V.; Padmaperuma, A. B.; Lemmo, T. Acid Number Determination of Pyrolysis Bio-Oils Using Potentiometric Titration; **Technical Report NREL/TP-5100-65890**. March 2, 2016.
- [4-30] van de Beld, B.; Heeres, H.; Somers, B.; Han, J.; Ferrari, F.; Goodfuels, M. Hydrotreated Pyrolysis Oil for Marine Application: Fuel Production and Combustion Performance. **IEA Bioenergy, Task 34**, 2022. https://task34.ieabioenergy.com/wp-content/uploads/sites/3/2022/12/Pyne52_complete.pdf (accessed 2024-05-26).
- [4-31] Oasmaa, A.; Leppamäki, E.; Koponen, P.; Levander, J.; Tapola, E. Physical Characterisation of Biomass-Based Pyrolysis Liquids Application of Standard Fuel Oil Analyses; Espoo, 1997. <http://www.vtt.fi/inf/pdf/publications/1997/P306.pdf> (accessed 2024-08-09).
- [4-32] Aakko-Saksa, P. et al. Synthesis of potential fuels for combustion engine power plants (**FCEP WP4 report D4.3**) (2014)
- [4-33] K.J. Chong, A.V. Bridgwater Fast Pyrolysis Oil Fuel Blend for Marine Vessels **Environ Prog Sustain Energy**, 36 (2017), pp. 677-684, 10.1002/ep.12402
- [5-1] Sudan Reddy Dandu, M. and K. Nanthagopal, *Tribological aspects of biofuels – A review*. **Fuel**, 2019. 258: p. 116066.
- [5-2] Dutcher DD et. Al. "Emissions from Ethanol-Gasoline Blends: A Single Particle

Perspective". **Atmosphere**, 2, 182-200, 2011.

[5-3] Agarwal, A.K., et al., *Toxicity of exhaust particulates and gaseous emissions from gasohol (ethanol blended gasoline)-fuelled spark ignition engines*. **Environmental Science: Processes & Impacts**, 2020. 22(7): p. 1540-1553.

[5-4] Maricq, MM. "Soot formation in ethanol/gasoline fuel blend diffusion flames". **Combustion and Flame**, 159(1), p. 170-180, 2012.

[5-5] dos Santos Filho D et. al. "Effects of ethanol content on cast iron cylinder wear in a flex-fuel internal combustion engine – A case study" **Wear** 406-407, 105-117, 2018.

[5-6] Costa, H.L. and H. Spikes, "Effects of Ethanol Contamination on Friction and Elastohydrodynamic Film Thickness of Engine Oils". **Tribology Transactions**, 2015. **58**(1): p. 158-168.

[5-7] Banerji, A et. al. "Friction reduction mechanisms in cast iron sliding against DLC: Effect of biofuel (E85) diluted engine oil". **Wear**, 2016. 368-369: p. 196-209.

[5-8] Bandeira, A.L., et al., "Sliding wear and friction behavior of CrN-coating in ethanol and oil–ethanol mixture". **Wear**, 2013. 301(1): p. 786-794.

[5-9] Khuong, LS, et al. "Effect of gasoline–bioethanol blends on the properties and lubrication characteristics of commercial engine oil". **RSC Advances**, 2017. **7**(25): p. 15005-15019.

[5-10] Khuong LS et. Al. "A review on the effect of bioethanol dilution on the properties and performance of automotive lubricants in gasoline engines" **RSC Advances**, 6, 66847-66869, 2016.

[5-11] Wicker R et. Al. "Practical Considerations for an E85-fueled Vehicle conversion" **SAE Technical Paper**, 1999.

[5-12] Shanta SM et. Al. Tribological Effects of Mineral-Oil Lubricant Contamination with Biofuels: A Pin-on-Disk Tribometri and Wear Study". **Adv. Trib.**, 2011, 820795, 2011.

[5-13] Boons M et. Al. "The impact of E85 use on lubricant performance". **SAE paper** 2008. 2008-01-1763.

[5-14] Schwartz SE "Observations Through a Transparent Oil Pan During Cold-Start, Short-Trip Service". 1991, **SAE International**, 1991.

[5-15] Chui GK et. Al. "Lubrication behaviour in ethanol-fueled engines" **Proceedings of the 4th Symposium on Alcohol Fuels**. Guruja, Brazil, 5-8 October 1980.

[5-16] Chui GK and Millard DHT. "Development and testing of crankcase lubricants for alcohol fueled engines". **SAE paper** 811203, 1981.

[5-17] Khalifa GA. "Effect of hydrous ethanol on crankcase oil dilution (carburetion,

fumigation)". **Oregon State University**. p. 160, 1985.

[5-18] Crepaldi J et. Al. "A New Tribology Test Procedure to Investigate Ethanol Dilution on Ethanol Engines". **SAE Technical Papers**, 0148-7191, 2018.

[5-19] Taylor RI. "Fuel-Lubricant Interactions: Critical Review of Recent Work" **Lubricants**, 2021. **9**(9): p. 92.

[5-20] Calabokis OP, et al. "Effect of an Aftermarket Additive in Powertrain Wear and Fuel Consumption of Small-Capacity Motorcycles: A Lab and Field Study". **Lubricants**, 2022. **10**(7): p. 143.

[5-21] Tippayawong N and Sooksarn P. "Assessment of lubricating oil degradation in small motorcycle engine fueled with gasohol". **Int. J. Sci. Technol.**, 4, 201-209, 2010.

[5-22] Ajayi OO et. Al. "Bioderived Fuel Blend Dilution of Marine Engine Oil and Impact on Friction and Wear Behavior" **J. Tribol.**, 138, 021603, 2015.

[5-23] Wu Y et. Al. "Oxidative degradation of synthetic ester and its influence on tribological behavior" **Tribol. Int.**, 64, 16-23, 2013.

[5-24] De Feo M et al. "Ageing impact on tribological properties of MoDTC-containing base oil". **Tribology International**, 2015. 92: p. 126-135.

[5-25] Costa HL et. Al. "Use of XANES and XPS to investigate the effects of ethanol contamination on anti-wear ZDDP tribofilms" **Tribol. Int.**, 159, 106997, 2021.

[5-26] Cousseau T et. Al. "Tribological response of fresh and used engine oils: The effect of surface texturing, roughness and fuel type". **Tribology International**, 2016. **100**: p. 60-69.

[5-27] Ruiz-Acero JS et al. "The effect of ethanol fuel dilution on oil performance and MoDTC tribofilm formation and composition Friction", 2023. **Under review**.

[5-28] Costa HL et. Al. "Current Knowledge on Friction, Lubrication and Wear of Ethanol-Fuelled Engines – A Review". **Lubricants**, 11, 292, 2023.

[5-29] De Feo M et. Al. "MoDTC friction modifier additive degradation: Correlation between tribological performance and chemical changes". **RSC Adv.** ,5, 93786-93796, 2015.

[5-30] Costa HL and Spikes H. "Effects of Ethanol Contamination on Friction and Elastohydrodynamic Film Thickness of Engine Oils". **Tribology Transactions**, 2015. **58**(1): p. 158-168.

[5-31] Costa HL and Spikes H "Interactions of Ethanol with Friction Modifiers in Model Engine Lubricants". **Lubricants**, 2019. **7**(11): p. 101.

[5-32] Costa HL and Spikes HA. "Impact of ethanol on the formation of antiwear tribofilms from engine lubricants". **Tribology International**, 2016. 93, Part A: p. 364-376.

- [5-33] De Silva PR et. Al. "Tribometer investigation of the frictional response of piston rings with lubricant contaminated with the gasoline engine biofuel ethanol and water" **Proc Inst. Mech. Eng. Part J. J. Eng. Tribol.**, 225, 347-358, 2011.
- [5-34] Kumar V and Agarwal AK "Friction, Wear, and Lubrication Studies of Alcohol-Fuelled Engines" in **Advances in Engine Tribology**, V. Kumar, et al., Editors. 2022, Springer Singapore: Singapore. p. 9-29.
- [5-35] Besser C., et al. "Investigation of long-term engine oil performance using lab-based artificial ageing illustrated by the impact of ethanol as fuel component". **Tribology International**, 2012. **46**(1): p. 174-182.
- [5-36] Gaffney JS and Marley NA, "The impacts of combustion emissions on air quality and climate – From coal to biofuels and beyond". **Atmospheric Environment**, 2009. **43**(1): p. 23-36.
- [5-37] Lenauer C et al. "Piston ring wear and cylinder liner tribofilm in tribotests with lubricants artificially altered with ethanol combustion products". **Tribology International**, 2015. **82**: p. 415-422.
- [5-38] Oguma M et. Al. "Evaluation of hydrous ethanol fuel lubricity by HFRR". **SAE Technical Papers**, 2016
- [5-39] Dubois T et. Al. "Investigating the Impact of Ethanol on the Lubricity of Gasoline and on the Lubricity Improvers Efficiency". **SAE Technical Papers**, 2017.
- [5-40] Shirani A et. Al. "Mechanochemically driven formation of protective carbon films from ethanol environment". **Mater. Today Chem.**, 26, 101112, 2022.
- [5-41] Dias LC et. al., "ZDDP Tribofilm Formation from a Formulated Oil on Textured Cylinder Liners". **Lubricants**, 2022. 10(6): p. 118.
- [5-42] Zhang J and Spikes H "On the mechanism of ZDDP antiwear film formation" **Tribol. Lett.**, 63, 24, 2016.
- [5-43] Pereira G et. al. "The role of the cation in antiwear films formed from ZDDP on 52100 steel". **Tribology Letters**, 2006. 23(2): p. 109-119.
- [5-44] Martin JM "Antiwear mechanisms of zinc dithiophosphate: A chemical hardness approach". **Tribol. Lett.**, 6, 1-8, 1999.
- [6-1] J.T. Gray, E. Dimitroff, N.T. Meckel, J.R. Quillian, Ammonia fuel-engine compatibility and combustion, **SAE Technical Paper** 660156 (1966). [https://doi.org/ 10.4271/660156](https://doi.org/10.4271/660156)
- [6-2] A. Valera-Medina, H. Xiao, M. Owen-Jones, W.I.F. David, P.J. Bowen, Ammonia for power, **Prog. Energy Combust. Sci.** 69 (2018) 63–102, [https://doi.org/ 10.1016/j.pecs.2018.07.001](https://doi.org/10.1016/j.pecs.2018.07.001).
- [6-3] P. Dimitriou, R. Javaid, A review of ammonia as a compression ignition engine fuel,

Int. J. **Hydrogen Energy** 45 (11) (2020) 7098–7118

[6-4] J. Lasocki, M. Bednarski, M. Sikora, Simulation of ammonia combustion in dual-fuel compression-ignition engine, **IOP Conf. Series-Earth Environ. Sci.** 214 (2019), 012081

[6-5] Cole-Parmer Instrument Company. Chemical compatibility database, 2017. Available online <https://www.coleparmer.co.uk/Chemical-Resistance> (Accessed at 09 November 2021).

[6-6] Y. Shen, S.M. Moghadam, F. Sadeghi, K. Paulson, R.W. Trice, Effect of retained austenite-compressive residual stresses on rolling contact fatigue life of carburized AISI 8620 steel, **Int. J. Fatigue** 75 (2015) 135–144.

[6-7] K. Ryu, G.E. Zacharakis-Jutz, S.C. Kong, Effects of gaseous ammonia direct injection on performance characteristics of a spark-ignition engine, **Appl. Energy** 116 (2014) 206–215.

[6-8] Teknological Institute Denmark. Personal communication.

[6-9] Agocs, A et. Al. “The Impact of Ammonia Fuel on Marine Engine Lubrication: An Artificial Lubricant Ageing Approach”. **Lubricants** 2023, 11, 165.

[6-10] R.P.M. Procter, M.V.E. Omideyi, R.C. Newman, Z. Wenyue, Stress-corrosion cracking of C-Mn steels in methanol-ammonia environments-I. Effects of environmental and mechanical variables, **Corrosion Sci.** 33 (7) (1992) 1009–1031

[6-11] D.C. Agarwal, Effect of ammonia concentration on environment-assisted failures in a low-nickel copper alloy, **Pract. Fail. Anal.** 3 (2003) 58–68.

[6-12] K.W. Gao, W.Y. Chu, H.L. Li, Y.P. Liu, L.J. Qiao, Correspondence between hydrogen enhancing dezincification layer-induced stress and susceptibility to SCC of brass, **Mater. Sci. Eng. A-Struct. Mater. Propert. Microstruct. Processing** 371 (1–2) (2004) 51–56.

[6-13] B. Garrett, Findings of hydrogen internal combustion engine durability, Final technical/scientific report, Office of Scientific and Technical Information (2010).

[6-14] D. Oh, J.S. Plante, A highly efficient small-displacement marine two-stroke H2DI engine with low emissions, **J. Eng. Gas Turbines Power-Trans. ASME** 135 (8) (2013), 082001.

[6-15] S. Verhelst, R. Sierens, Hydrogen engine-specific properties, **Int. J. Hydrogen Energy** 26 (9) (2001) 987–990.

[6-16] R. Mathai, R.K. Malhotra, K.A. Subramanian, L.M. Das, Comparative evaluation of performance, emission, lubricant and deposit characteristics of spark ignition engine fueled with CNG and 18% hydrogen-CNG, **Int. J. Hydrogen Energy** 37 (8) (2012) 6893–6900.

[6-17] J.W. Jones, J.J. Wert, The effects of gaseous environments on the wear of

commercial purity titanium, **Wear** 32 (3) (1975) 363–377.

[6-18] E.P. Georgiou, V.P. Cevallos, T. Van der Donck, D. Drees, J. Meersschaut, C.N. Panagopoulos, J.P. Celis, Effect of cathodic hydrogen charging on the wear behavior of 5754 Al alloy, **Wear** 390–391 (2017) 295–301.

[6-19] D. Landolt, S. Mischler, Tribocorrosion of passive metals and coatings, **Woodhead Publishing**, UK, 2011.

[6-20] L. Grunberg, D.T. Jamieson, D. Scott, Hydrogen penetration in water-accelerated fatigue of rolling surfaces, **Wear** 7 (5) (1963) 474.

[6-21] Semelsberger, T.A., Borup, R.L. and Greene H.L. (2006) Dimethyl ether (DME) as an alternative fuel. **Journal of Power Sources** 156 (2006) 497–511.

[6-22] Sivebaek, I. M. (2001) End-Report of Task 20 of the IEA-AMF of the IEA: 'DME as an Automotive Fuel II', Part 2, **DTU MEK-ET-ES** 2001-04.

[6-23] Lim, O. et al. (2010) Research on the combustion and emission characteristics of the DME/Diesel Dual-Fuel engine. **SAE Technical Paper** 2010-32-0096.

[6-24] Jung, D., Jeong, J., Lim, O. and Pyo, Y. (2011) Influence of pilot injection on combustion characteristics and emissions in a DI diesel engine fuelled with diesel and DME. **SAE Technical Paper** 2011-01-1958.

[6-25] Zhang, G., et al. (2012) Study on strategies of anti-wear and leakage for fuel injection system of dimethyl ether (DME) engine. Society of Automotive Engineers. **SAE Technical Paper** 2012-32-0073.

[6-26] Kapus, P. and Ofner, H. (1995) Development of Fuel Injection Equipment and Combustion System for DI Diesels Operated on Dimethyl Ether, **SAE Technical Paper** 950062.

[6-27] Van der Ploeg, C.T.M. and Verbeek R.P. (2002) End-Report of Task 20 of the IEA-AMF of the IEA: 'DME as an Automotive Fuel II', Part 1. **TNO report**.