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Diese Dissertation haben begutachtet:
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DISSERTATION

Impact of bio-ethanol as oxygenated fuel component in gasoline on the engine oil performance

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Margarethen am Moos, März 2015

To my parents, my grandparents,
and my beloved darling

– Nam idem velle atque idem nolle,
ea demum firma amititia est –
(C. Sallustius Crispus: De Catilinae coniuratione)

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Abstract

Due to legislative issues, the admixture of bio-components to fossil fuels for combustion engines – i.e. ethanol in gasoline and fatty acid methyl esters (bio-diesel) in diesel – has come up in the last decades. Bio-diesel and its impact on the engine performance, the emission profile as well as the lubrication system have been intensively investigated, whereas the effect of ethanol and its partial combustion products is widely unclear.

In the course of this thesis, the development of a novel lab-based artificial alteration method especially designed to simulate strains occurring in bio-ethanol fuelled automotives and the results thereof are presented. Artificial alteration of three fully formulated engine oils with addition of ethanol, acetaldehyde, and acetic acid was carried out. It was shown that ethanol as well as acetaldehyde has almost no effect on the oil degradation especially in the case that advanced additive technology was used. On the contrary, acetic acid significantly affected the formulated oil showing influence on the detergent chemistry and even caused sludge formation. The use of the novel artificial alteration method proved to clearly differentiate the impact of the respective compounds combined with the possibility to simulate enhanced stress conditions without the need of time-consuming and expensive engine bench tests, hence, offering valuable input for the formulation and the pre-selection of future engine oils suitable for bio-fuel application.

As a consecutive step, oils evaluated in the laboratory were subjected to a chassis dynamometer bench test for examination under more realistic conditions. In addition to reference runs, bench tests were performed with addition of acetic acid to the oil circuit. Oil condition monitoring enabled the differentiation between runs with and without addition of acid. Moreover, interaction of the oils with acetic acid could be differentiated attributed to different oil formulations. Optical emission spectroscopy of oil samples collected during condition monitoring provided an indication of an elevated corrosion potential towards iron and copper when adding acetic acid although this contamination has been largely evaporated during the bench tests. However, failure assessment by scanning electron microscopy of used parts demounted from the passenger car after the bench tests showed no significant signs of corrosion or mechanical wear giving evidence for material ablation. As corroboration of these findings, static corrosion experiments were performed in the laboratory with good correlation to results obtained from the chassis dynamometer bench test.

As concluding investigation, data achieved during artificial alteration in the laboratory were compared with findings during chassis dynamometer bench tests by joint use of fourier transformation infrared (FTIR) spectroscopic data and chemometrics. Quantification of residual amounts of antioxidant and antiwear additive (zinc dithiophosphate) in the oil samples by FTIR spectroscopy showed depletion of phenolic antioxidant during engine alteration but zinc dithiophosphate degradation during artificial alteration. The chemometric method principal component analysis (PCA) elucidated similarities and differences between both alteration types, verifying the findings of FTIR spectroscopy. Additionally, it was found, that laboratory-based artificial alteration was mainly driven by oxidative processes whereas engine alteration showed higher amounts of both oxidation and nitration products.

Zusammenfassung

Aufgrund gesetzgebender Maßnahmen erfuhr die Beimengung von Substanzen, die aus erneuerbaren Rohstoffen gewonnen werden, zu fossilen Kraftstoffen für Verbrennungsmotoren – Ethanol (Bioethanol) zu Benzin und Fettsäuremethylester (Biodiesel) zu Dieselkraftstoff – in den letzten Jahrzehnten einen großen Aufschwung. Biodiesel sowie sein Einfluss auf die Motorleistung, das Emissionsprofil und das Schmiersystem wurden bereits intensiv untersucht, wohingegen der Effekt von Ethanol und seinen partiellen Verbrennungsprodukten noch weitgehend unklar ist.

Im Zuge dieser Arbeit werden die Entwicklung einer neuen künstlichen Alterungsmethode, speziell konzipiert zur Simulation von Belastungen, die in einem mit bioethanolhältigem Kraftstoff betankten Auto auftreten können, sowie Ergebnisse davon präsentiert. Durch künstliche Alterungen von drei vollformulierten Motorölen mit der Beifügung von Ethanol, Acetaldehyd und Essigsäure konnte gezeigt werden, dass sowohl Ethanol als auch Acetaldehyd so gut wie keinen Effekt auf die Ölalterung haben, im Besonderen bei Ölen mit modernen Additivtechnologien, wohingegen die Essigsäure einen signifikanten Einfluss auf Ölstabilität aufweist und sogar zu Schlammbildung führt. Der Einsatz der neuen künstlichen Alterungsmethode bewies, dass eine klare Differenzierung des Einflusses einzelner Komponenten bei der Simulierung erhöhter Stressbedingungen ohne den Aufwand von zeit- und kostenintensiven Motorprüfstandstests möglich ist. Damit wird ein wertvoller Beitrag zur Formulierung und Vorauswahl zukünftiger Motoröle mit erhöhter Verträglichkeit hinsichtlich Biokraftstoffkomponenten geleistet.

Als weiterführender Schritt wurden bereits im Labor evaluierte Öle auf einem Rollenprüfstand eingesetzt, um sie unter realistischeren Bedingungen zu untersuchen. Zusätzlich zu Referenzläufen wurden auch Prüfstandsläufe mit der Beifügung von Essigsäure zum Ölkreislauf durchgeführt. Ölzustandsanalysen ermöglichten nicht nur eine Differenzierung zwischen Läufen mit und ohne Essigsäurezugabe, sondern auch eine Unterscheidung der Interaktion der Öle mit der Essigsäure je nach Formulierung. Optische Emissionsspektroskopie von Ölproben, die im Zuge der Zustandsanalysen gezogen wurden, gaben weiters Hinweis auf ein erhöhtes Korrosionspotential der Öle gegenüber Eisen und Kupfer bei der Zugabe von Essigsäure, obwohl diese während der Testläufe weitgehend in die Gasphase übergeführt wurde. Trotzdem ergab eine Untersuchung mittels Rasterelektronenmikroskopie von gebrauchten Motorbauteilen aus dem Rollenprüfstand keine signifikanten Anzeichen für Korrosion oder mechanischen Verschleiß und somit für einen

Materialabtrag. Zur Untermauerung dieser Erkenntnisse wurden statische Korrosionsexperimente im Labor durchgeführt, die eine gute Korrelation zu Ergebnissen aus den Prüfstandtests zeigten.

Als abschließende Untersuchung wurden infrarotspektroskopische Daten aus der künstlichen Alterung im Labor mit jenen aus den Rollenprüfstandtests mittels eines chemometrischen Ansatzes – PCA – verglichen. Die Quantifizierung der Restmengen an Antioxidantien und Verschleißschutzadditiven (Zinkdithiophosphat) in den Ölproben durch Infrarotspektroskopie zeigte einen Abbau von phenolischen Antioxidantien während der Ölalterung im Rollenprüfstand, jedoch eine Abnahme von Zinkdithiophosphat während der künstlichen Alterung im Labor. Durch PCA (Hauptkomponentenanalyse) wurden Ähnlichkeiten und Unterschiede zwischen beiden Alterungstypen aufgezeigt. Zusätzlich wurde herausgefunden, dass die künstliche Alterung im Labor hauptsächlich durch oxidative Prozesse bedingt ist, wohingegen durch die Alterung im Rollenprüfstand hohe Mengen sowohl an Oxidations- als auch an Nitrationsprodukten entstehen.

Table of content

PART A: Introduction 11
1. Bio-fuels 11
1.1. First generation bio-fuels 13
1.2. Second generation bio-fuels 15
1.3. Third generation bio-fuels 17
1.4. Fourth generation bio-fuels 18
1.5. Legislative issues 19
2. Engine oils 23
2.1. Functions and properties of engine oils 23
2.2. Engine oil composition 25
2.2.1. Base oils 25
2.2.2. Additives 27
2.2.2.1. Antioxidants 27
2.2.2.2. Detergents 28
2.2.2.3. Dispersants 29
2.2.2.4. Antiwear and extreme pressure additives 31
2.2.2.5. Viscosity modifiers 32
2.2.2.6. Pour point depressants 33
2.2.2.7. Foam inhibitors 33
3. Analytical methods for engine oils 35
3.1. Fresh oil parameters 35
3.1.1. Viscosity and viscosity index 35
3.1.2. Total Base Number (TBN) 38
3.1.3. Neutralization Number (NN) or Acid Number (AN) 39
3.1.4. Saponification Number (SN) 40
3.1.5. Flash point 40
3.1.6. Pour point 41
3.2. Oil alteration parameters 41
3.2.1. Appearance (colour and transparency) and odour 42
3.2.2. Change in viscosity behaviour 42
3.2.3. Fourier Transform - Infrared spectroscopy (FT-IR) 43
3.2.3.1. Detection of oil degradation by oxidation, nitration, and sulfation 44

3.2.3.2. Detection of contamination built-up by water and soot 45
3.2.3.3. Additive content 46
3.2.4. Change in TBN, NN, and AN 47
3.2.5. Optical emission spectroscopy with inductively coupled plasma (ICP-OES) . 47
4. Oil alteration 53
4.1. Mechanism of oxidation 53
4.1.1. Chain initiation 53
4.1.2. Chain propagation 54
4.1.3. Chain branching 54
4.1.4. Chain termination 55
4.2. Currently applied standards 55
4.2.1. General standards 55
4.2.1.1. Thermo-oxidative methods at ambient pressure 55
4.2.1.2. Thermo-oxidative methods under pressure 58
4.2.1.3. Thermo-oxidative methods with catalysts 60
4.2.1.4. Thermo-oxidative methods under pressure and with catalysts 65
4.2.2. Standards for engine oils 67
5. Chemometrics as data processing tool 75
PART B: Experimental, results, and conclusions 82
1. Objective target of the thesis 82
2. Publications within the thesis topic 83
2.1. Investigation of long-term engine oil performance using lab-based artificial ageing illustrated by the impact of ethanol as fuel component 83
2.2. Impact of engine oil degradation on wear and corrosion caused by acetic acid evaluated by chassis dynamometer bench test 93
2.3. Comparison of engine oil degradation observed in laboratory alteration and in the engine by chemometric data evaluation 107
3. Conclusions 119
4. Curriculum vitae 123

PART A: Introduction

1. Bio-fuels

Throughout man's history, bio-fuels have been used, mostly in the form of alcohol produced by fermentation of starch or sugar-containing biomass but also plant oils. [1.1] Besides that, energy commodities such as wood and wood coal, wind mills, water mills, and animals (horses, oxen) came into operation.

Although coal entered into industrial processes in the course of the Industrial Revolution which started in the late 18th century, it was not until the beginning of the 19th century, when the focus of research and development was laid on fossil feedstock represented by petroleum, coal, and natural gas. On the base thereof, a variety of industrial goods are being produced: fuels, fine chemicals, pharmaceuticals, detergents, synthetic fibres, plastics, pesticides, fertilizers, lubricants, solvents, waxes, coke, asphalt, etc.

However, the intense use of fossil sources makes (again) necessary the need and search for alternatives. Significant economic as well as environmental concerns are:

- Growing world population leading to an increasing demand of energy
- Reduction of the worldwide mineral oil resources resulting in rising prices of crude oil
- Reliability of supply endangered
- Political instabilities in the major producing countries
- Dependence on foreign petroleum resources
- Ozone layer depletion
- Elevated greenhouse gas emissions (e.g. carbon dioxide and methane) connected with global warming

Out of these reasons, the research for sustainable, environmentally benign, renewable, efficient, and cost-effective feedstock for energy production for both industrial use and consumer societies has significantly increased in the last decades. The need for vehicles with a low carbon footprint and transportation fuels with a high energy density should be – among other measures – satisfied by fuels produced from biomass consisting of photosynthesis-fixed carbon [1.1-1.7].

Figure 1 depicts the increasing bio-fuel production worldwide and by region in the last decade (left diagram). It can clearly be seen, that the boom in the production of bio-fuels started in the years 2004 to 2006. At the time of publication, it was expected that this rising tendency shall be maintained in the next decades (Figure 1 right diagram) as shown for the future

prospect of the bio-fuel production in the United States until the year 2022 according to the target defined in the Energy Independence and Security Act (EISA) in 2007 [1.6].

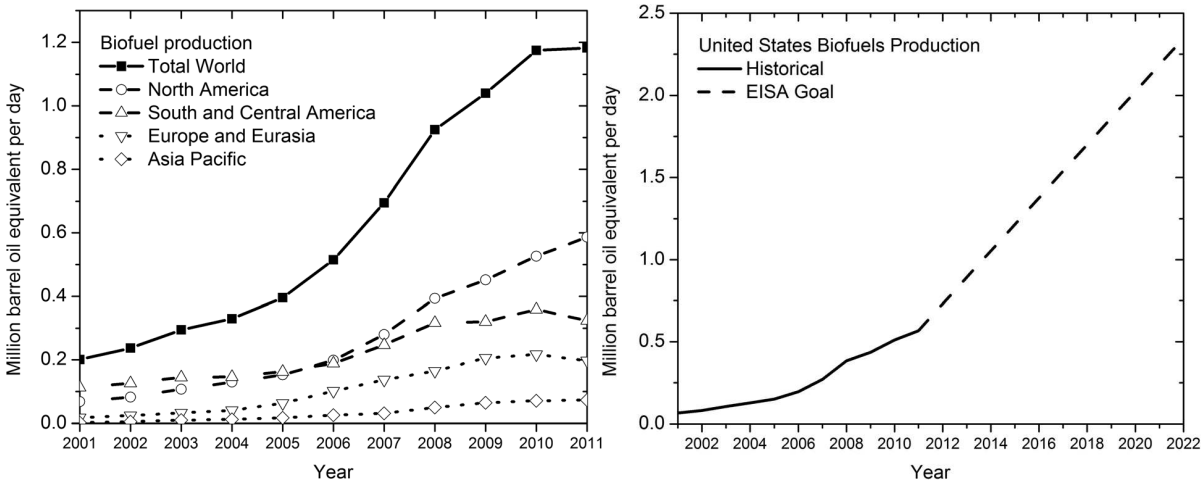

Figure 1: Bio-fuel production by region in the years 2001 to 2011 (left); projected bio-fuel production in the United States until 2022 (right) based on the Energy Independence and Security Act target [1.6]

Bio-fuels are classified in four generations according to their feedstock and production technology. Figure 2 gives an overview over the different groups of bio-fuels, their feedstock, and their methods of synthesis.

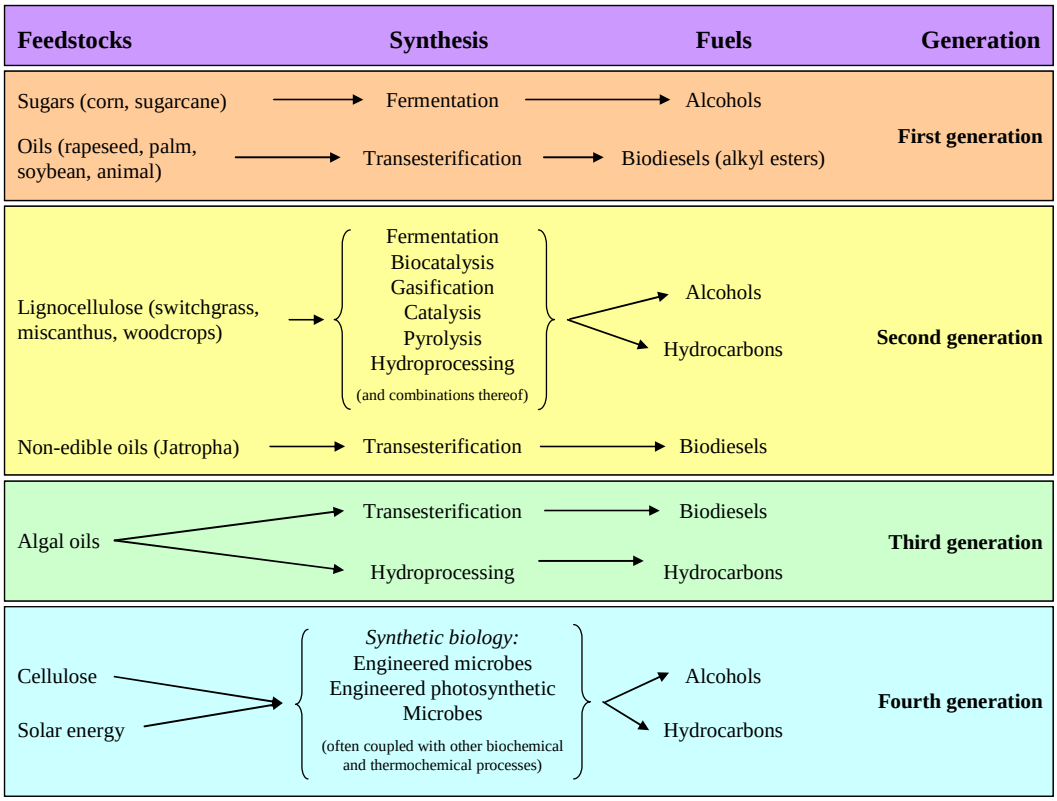

Figure 2: Generations of bio-fuels, their feedstock and production pathways [1.6]

The individual generations of bio-fuels regarding their production, benefits and shortcomings, are discussed in detail in the following sub-chapters.

1.1. First generation bio-fuels

Bio-fuels of the first generation form almost 100 % of the current bio-fuel market. Large quantities thereof are produced world wide by conventional techniques of **production**, so-called “established technologies”.

In the broad public, the term “bio-fuel” is connected mainly with bio-ethanol as gasoline substitute and the methyl esters of fatty acids in bio-diesel. Besides that, bio-fuels include a big variety of chemical compounds. Generally, there are three main types, commercially very successful [1.2, 1.5 - 1.9]:

1. Fatty acid methyl ester (FAME), also known as bio-diesel, is produced by transesterification of vegetable oils, residual oils, and animal fat. Dependent on the region, different main resources are employed. In the United States, the main commodity is soybean, whereas in Europe basically rapeseed is used for bio-diesel production. In Asia (primarily in Malaysia), bio-diesel is made from palm oil.
2. Bio-alcohols are manufactured by fermentation of starches and sugar by enzymes and micro-organisms. The most common type produced worldwide is ethanol, which can be used up to 100 °% as gasoline substitute in so-called flexi-fuel vehicles. Ethanol is also base product for ethyl tertiary butyl ether (ETBE), another oxygenated blending product for gasoline. Furthermore, butanol can be used directly in many gasoline engines.

   The United States and Brazil are the world’s largest bio-ethanol producers with ~ 9 billion and 6.5 billion gallons per year, respectively. According to climatic factors, the commodities vary from region to region. In the United States, the main feedstock for bio-ethanol is corn, whereas ethanol production in Brazil is based on sugarcane. In Europe, crops like wheat, barley, rye, and corn are used as well as sugar beets or wastes from wine-making.
3. Bio-gas, the third widely-used bio-fuel type, is produced by anaerobic digestion of organic mass either from biodegradable waste or from energy crops. It contains high concentrations of methane and is burnt in special stationary gas engines, hence converting it to electricity and heat. In addition, its solid by-product accumulating during bio-gas formation can also be used as bio-fuel or brought back on agricultural areas as fertilizer.

Figure 3 and Figure 4 give an overview over the commodities bio-diesel and bio-ethanol production in Europe and in the United States.

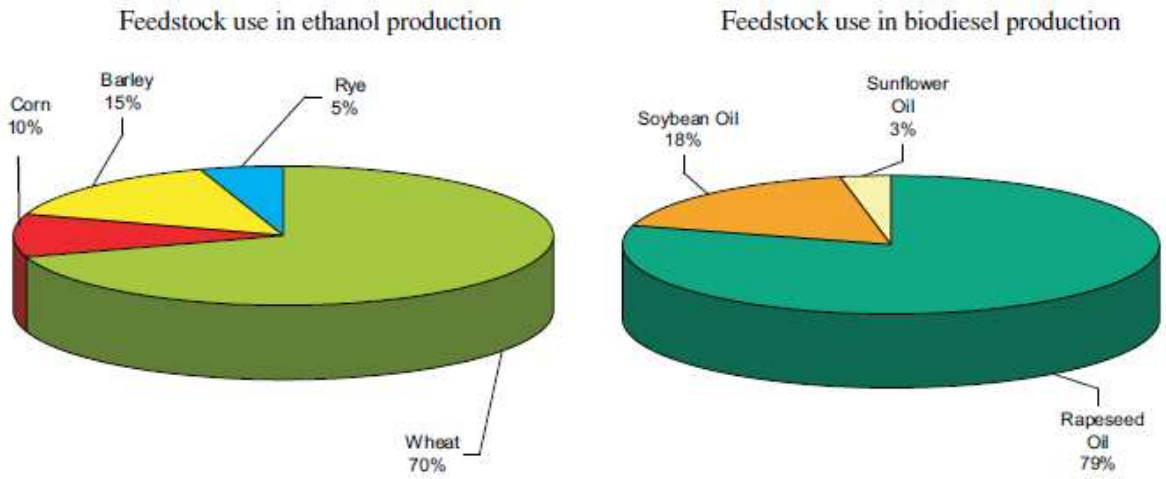

Figure 3: Resources for bio-fuel production in Europe in 2008 [1.7]

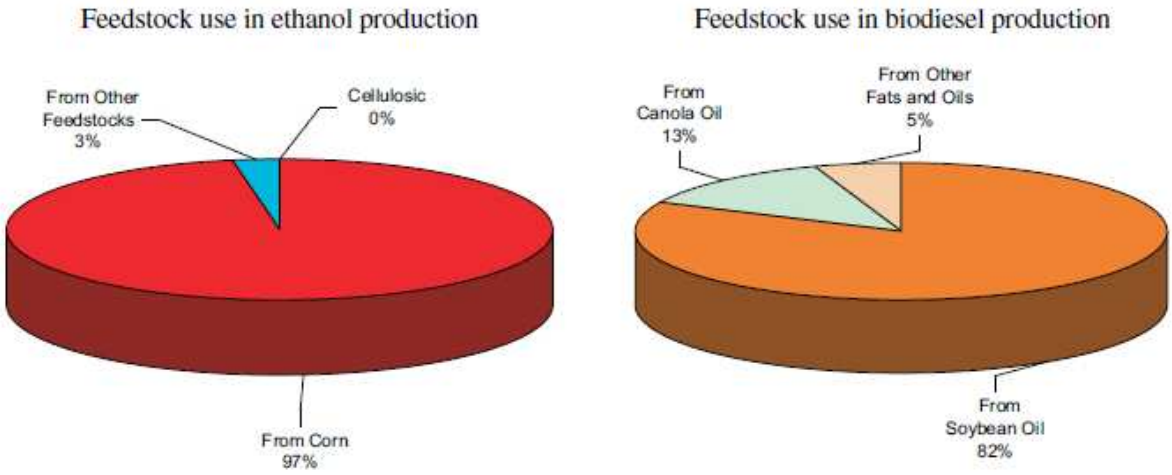

Figure 4: Resources for bio-fuel production in the United States in 2008 [1.7]

The **main benefits** of this generation of bio-fuels are the major reasons for their application and their resounding success resulting in a widespread adoption [1.2, 1.5, 1.6, 1.8 - 1.10]. At the first sight, they offer a solution for almost all issues which led to the development of bio-originating fuels:

- They are easily available and at reasonable costs (cheap).
- They exhibit a high degree of environmental friendliness as well as economic feasibility.

- They are considered as effective alternatives to transportation fuels based on fossil feedstock due to the long-term possibility of fuel-source regenerability combined with the reduction of a climatic impact.
- Social security is improved in terms of support for agricultural industries and rural communities.
- The oil import can be reduced resulting in a higher independency from foreign oil exploring countries.

Besides all positive effects and benefits of bio-fuels of the first generation, also **shortcomings** occur in connection with their application resulting in public controversy [1.2, 1.5 - 1.9, 1.11]. The major concern in this context is the so-called food-versus-fuel debate. The increasing production of bio-fuels from crops provoked a reduced availability of food supply at the international market resulting in rising food prices.

In addition, their ability for the total replacement of fossil fuels is put into question due to fact that even all available organic commodities, such as crops, wood, and grasses, would not be sufficient to result in full independency from mineral fuels.

Furthermore, scepticism about their environmental impacts and carbon balance as well as about their social implications arose. Environmental issues include the expanding soil erosion and water pollution by fertilizers and pesticides with increasing bio-fuel production, as well as the extending effort in agriculture due to higher energy and water demand combined with considerable land usage. They contribute to a more frequent appearance of monocultures and deforestation as well as to the NO_x-gas production during combustion due to their uptake of nitrogen containing fertilizers. These issues may lead to the fact, that more and more critics question the real sustainability of bio-fuels of the first generation.

The trend is going towards the commercial-scale development as well as augmented application of second and third generation bio-fuels in order to overcome the shortcomings of bio-fuels of the first generation. [1.4]

1.2. Second generation bio-fuels

Shortcomings of first generation bio-fuels led to increased attention paid to the development of alternatives based on non-food commodities and/or on the utilization of agriculture residues in combination with a lower demand of land and water resources, commonly known as bio-fuels of the second generation. These so-called “advanced bio-fuels” are presently at the scale-up stage of commercialisation.

The main differentiating factor between bio-fuels of the first and second generation is their origin. Generally, the **production** of second generation bio-fuels is based on cheap, non-food crops or residual biomass which accrues as waste product in food industry, e.g. waste vegetables [1.5, 1.6, 1.11 - 1.13].

Typical resources are:

- Wood crops – short rotation forestry crops, e.g. poplar, willow, eucalyptus
- Lignocellulosic commodities – perennial grasses, e.g. miscanthus, switch grass, reed canary grass
- Waste from wood industry, forestry, and agriculture
- Non-edible oils, e.g. Jatropha

The production of second generation bio-fuels comprises different technologies than that of first generation due to different commodities. Examples therefore are:

- Ethanol production by hydrolysis and fermentation
- Fast pyrolysis, a thermochemical conversion process under heating in the absence of oxygen for the production of liquid bio-fuels
- Gasification for manufacturing Fischer-Tropsch bio-diesel, bio-dimethyl ether, and bio-synthetic natural gas
- Catalysis and biocatalysis
- Hydroprocessing

Compared to the first generation, bio-fuels of the second generation exhibit various **advantages** or rather they compensate shortcomings of the first generation [1.5, 1.9, 1.11, 1.13], such as

- Application of cheap and easily available commodities without competition with food, thus reducing the food-versus-fuel debate
- Higher sustainability and carbon neutrality or even carbon negativity regarding its CO_2 emission, hence reduction in greenhouse gas emission
- Utilization of raw material with high levels of lignin and cellulose content resulting in an increased effectiveness regarding its applicability in bio-energy production and hence turning it into a highly suitable feedstock due to its high carbon content
- Possibility of direct combustion for heat and electricity production
- Increase in bio-fuel yield in correlation with agricultural, energy, and water demand as well as land usage
- Opportunity of liquid bio-fuel production

- Mainly utilization of lignocellulosic material from plants, which is the most abundant resource
- Alternative source of revenue for farmers

Ranking among the **disadvantages** of second generation bio-fuels, some facts have to be mentioned [1.11, 1.12]. Currently, their production is not cost-effective due to technical issues, e.g. pyrolysis still exhibits technical challenges in terms of the improvement of yield and quality of the produced liquid bio-fuels and the energy efficiency enhancement of the entire process.

In addition, environmental concerns exist regarding the excess removal of agricultural residues which could have adverse effects on soil and crop production resulting from the importance of crop residues in terms of soil property and water conservation, soil productivity enhancement, or sequestering carbon in soils. Consequently, the possible reduction of recoverability in forest areas due to heavy usage of forest residues is a major concern. Economic apprehensions include the need of specially designed harvest equipment and storage systems, the comparably long start-up period of approximately 2 to 3 years until the start of a full production as well as the competition with current uses, e.g. in the case of forest residues.

1.3. Third generation bio-fuels

The very new term of “third generation bio-fuels” corresponds to components **produced by algae** [1.14, 1.15]. By this procedure, high photosynthetic efficiency and large yields can be combined with low resource input compared to traditional feedstock.

A high diversity of produced fuel can be reached due to two properties of algae:

1. Algae are able to produce hydrocarbons that can be chemically converted to diesel or components of gasoline.
2. Algae can be genetically modified for the direct production of various fuels: bio-diesel, methane, ethanol, butanol, vegetable oil, diesel fuel or gasoline.

The **benefits** of bio-fuels produced by algae are manifold [1.14, 1.15]. Examples therefor are:

- Algae are highly independent from the growing location. Cultivation can happen in various ways: open ponds, closed loops, or photobioreactors. Even salt water from the sea can be utilized. This leads to a large advantage that no farmland can offer.
- Algae can even be grown in waste water which depicts a secondary benefit by digestion of municipal sewage and contribution to water purification.
- A very broad range of carbon sources can be used by algae.

- The cultivation location can be directly connected to carbon emitting industries, thus enabling a direct conversion of emissions.

A **draw-back** of the comparably new technology of algae is related to its large-scale implementation due to the need of intensive research and development efforts connected with high investment costs [1.14, 1.15]. Thus, future forecasts act on the assumption that bio-fuels based on algae will be economically feasible only in about 25 years. An additional minor shortcoming is that bio-diesel produced from algae seems to possess lower stability than that from conventional commodities due to a higher content of unsaturated hydrocarbons. Furthermore, algae growth needs the dosage of high amounts of nitrogen and phosphorus, hence demanding the production of large amounts of fertilizers resulting in increased greenhouse gas emission.

1.4. Fourth generation bio-fuels

For the term "fourth generation bio-fuels", no formal definition exists. Some experts refer to it as "*the biofuels created from processes other than first generation ethanol and biodiesel, second generation cellulosic ethanol, and third generation algae biofuels*" [1.9].

Generally, bio-fuels of the fourth generation are produced by the application of advanced biochemical methods of **production** or modified organisms. They pursue not only the goal to produce sustainable energy but also they focus the capturing and storage of CO_2.

For example, bio-mass is genetically designed to exhibit a significantly higher CO_2 storage capacity compared to unmodified counterparts. This carbon rich organic compound is afterwards converted into fuel and gases by techniques applied also for second generation bio-fuels, i.e. pyrolysis, gasification, or digestion, with the difference, that at all production stages the CO_2 is captured and subsequently sequestered. This can happen in depleted oil and gas fields, saline aquifers, or coal mines. This procedure results in fuels, which are effectively carbon-negative due to the fact that more CO_2 is locked away than it is produced. Figure 5 gives a schematic overview over bio-fuels from genetically modified bio-mass [1.9, 1.16 - 1.18].

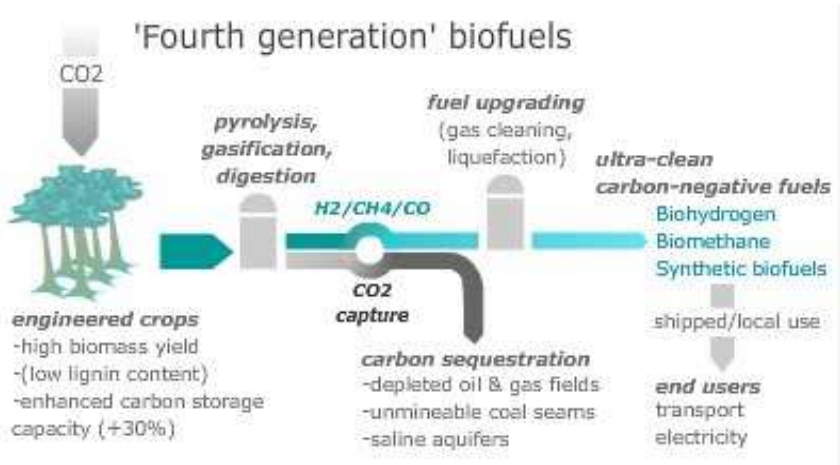

Figure 5: Schematic overview of bio-fuels from genetically modified bio-mass [1.18]

A second approach to bio-fuels of the fourth generation is the utilization of synthetic biological processes, such as the conversion of bio-mass to fuel (hydrocarbons or alcohols) by genetically manipulated, "engineered" microbes or the production of so-called "solar-fuels", when photosynthetic microbes convert CO_2, water, and sunlight directly to fuels [1.6, 1.9, 1.19]. A detailed insight in the production of solar fuels is given in [1.19].

Bio-fuels of the fourth generation possess the **potential** to even greater reduction of greenhouse gas emission and exhibit low land and energy usage compared to first, second, or third generation bio-fuels. Currently, they are under intense research and at the early stage of commercialization [1.6]. Especially photosynthetic systems require dramatic improvements regarding their efficiency and durability to consider them for wide-spread practical application [1.19]. Generally, fourth generation bio-fuels are highly forward-looking and – with enhanced efforts in research and development – may solve problems which arose by the utilization of first, second, and third generation bio-fuels.

1.5. Legislative issues

In order to accommodate the growing concerns causing the recent developments in the bio-fuel demand, many countries have taken up these issues in their legislation. In doing so, a big step forward should be done to replace a part of fossil fuels by bio-fuels.

At the homepage [1.20] of the hydrocarbon publishing group, a brochure is available with detailed information about statutory rules of various regions around the world. Due to the diversity of government regulations, this chapter only gives an overview over the legislative development in the European Union.

In 2003, the European Union began affiliating the usage of bio-fuel in its legislation. In the first step, the Directive 2003/30/EC [1.21] was released in May 2003, which was commonly

known as the “bio-fuels directive”. Therein, a replacement of 2 % of all fossil fuels related to the transportation sector by bio-fuels was proposed until December 31, 2005. Additionally, a further increase of substitution for up to 5.75 % was asked until December 31, 2010.

This non-binding directive was replaced in 2009 due to its limited success of implementation. Consequently, the European Parliament and the Council determined two major directives concerning the extended usage of renewable fuels until the year 2020, namely the Renewable Energy Directive 2009/28/EC (RED) [1.22] and an amended Fuel Quality Directive 2009/30/EC (FQD) [1.23].

As mandatory target, RED launches the replacement of at least 10 % of national energy demand in the transportation sector by renewable resources, i.e. renewable electricity, hydrogen, and sustainable bio-fuels, for all Member States. In 2010, the National Renewable Energy Action Plans (NREAP, see [1.24]) had to be submitted to the European Commission by all Member States, wherein they summarized their plans to achieve the claimed goals. NREAP specified that the target of 10 % replacement would be reached by 8.5 % conventional bio-fuels (first generation), 1 % bio-fuels of second generation, and 1 % renewable electricity (mostly used in railway transportation).

FQD demands a 6 % decrease of greenhouse gas emissions by all liquid fuels used in the transportation sector until the year 2020. In this directive, the permitted levels of emissions originating from fossil fuels are determined. Additionally, environmental criteria for components of fossil fuel, i.e. gasoline and diesel, as well as the amount and conditions of ethanol usage in gasoline (currently with the maximal concentration of 10 % ethanol) are defined [1.25 - 1.27].

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2. Engine oils

2.1. Functions and properties of engine oils

Engine oils fulfil various functions in order to maintain the proper operation of an engine. The **main requirements** are listed below [2.1].

1. Friction reduction

   The friction in the engine has to be reduced to decrease the energy requirements of a tribosystem. In addition, this lowers the local heat produced during the engine operation.

2. Wear reduction

   Minimising the occurring wear in a tribosystem is of particular importance to maintain the running of the equipment over a long period of time in an efficient manner.

3. Cooling

   The oil acts as an initial heat transfer agent between engine parts heated by combustion, i.e. pistons, cylinder liners, etc., and cooler regions for heat dissipation, i.e. the oil sump cooling jacket. In addition, heat generated by friction or the mechanical work performed is conveyed by the lubricant.

4. Corrosion protection

   By chemical mechanisms taking place during oil degradation as well as during combustion, acidic compounds are built, which can have a corrosive impact on metal engine parts. In humid environment or during periods of engine idleness, rusting of ferrous components is also facilitated. All these negative effects have to be prevented by the lubricant.

5. Cleanliness

   Similar to corrosion protection, the lubricant has to protect mechanical parts against fouling resulting on the one hand from oil degradation products such as solid carbon, varnish, and sludge, and on the other hand from combustion contamination by the prevention of deposit formation as well as by the dispersion of contaminations. Especially solid deposits can exert a negative impact on the proper operation of the engine. If the cleaning happens insufficiently by the oil, piston rings may become stuck or oil passages are blocked and hence cause severe engine damage.

6. Sealing

   Sealing between piston and cylinder, especially the contact from piston to piston rings and piston rings to cylinder liner walls, is of major importance for the operation of a combustion engine. The applied engine oil contributes to low blow-by gas.

In order to achieve these general requirements, engine oils have to exhibit **several distinct properties** as described below [2.1].

1. Appropriate viscosity-temperature properties

   The oil viscosity has to be high enough to prevent metal to metal contact and subsequently prohibit wear of machine parts. In addition, too low viscosity increases oil leakage. On the contrary, the oil viscosity has to be low enough to avoid starting difficulties especially at deep ambient temperatures and to minimise the loss of power. As a consequence, the lubricant has to exhibit a sufficiently high viscosity index to provide the required temperature-viscosity-behaviour of the engine oil.

2. Low volatility

   A high volatility means loss of oil and subsequently high oil consumption due to the evaporation of lighter oil components. Besides, the residual exhibits higher viscosity and evaporated oil easily causes deposit formation. Out of these reasons, engine oils should possess a low volatility.

3. Low foam building tendency

   Lubricants in engines should provide a low foam building tendency to avoid a loss of lubricating and cooling properties and – in severe cases – a loss of the oil itself by leakage.

4. High stability regarding oxidation and chemical attack

   Elevated temperatures in the engine as well as contamination by acids and other compounds imply a severe strain to the engine oil, which has to be highly stable towards these influences to preserve its desired properties.

5. Low impact on emission system components, coatings, and sealing material

   Unstable or degraded oils as well as unsuitable additive treatment may damage catalytic converters, hence decreasing their performance. Additionally, machine parts possibly carry paints, coatings, or elastomeric sealings. None of these components should be seriously attacked and subsequently harmed by the engine oil.

6. Low deposit forming tendency

   When coming in contact with hot metal parts, e.g. in the combustion chamber or in the ring zone, oil can decompose and develops oxidation products in the form of polymerized yellowish to brownish layers, known as varnish or lacquer. If such layers are built up, they could carbonize to solid carbon. Each type of these deposits can block machine parts which originally should be free to move, i.e. piston rings and therefore leads to severe

engine damage. Additionally, oil deposits in the combustion chamber may cause pre-ignition.

7. Low toxicity and pleasant odour

   For the comfort and the health of the user, engine oils should possess low toxicity as well as a pleasant odour.

8. Preferably low costs

   A real restraint is the demand for low-cost oils instead of advanced high-cost oils, which does not arise not from the point of engine operating economics but the competition between lubricant suppliers. Hence, there is a limited use of optimum lubricants due to limits regarding the acceptable ingredient costs.

2.2. Engine oil composition

2.2.1. Base oils

"Appendix E – API base oil interchangeability guidelines for passenger car motor oils and diesel engines" [2.2] in the "Engine Oil Licensing and Certification System" [2.3] of the American Petroleum Institute (API) defines a base stock as "*a lubricant component that is produced by a single manufacturer to the same specifications (independent of feed source or manufacturer's location); that meets the same manufacturer's specification; and that is identified by a unique formula, product identification number, or both*".

In doing so, various processes for base oil manufacturing are proposed, such as distillation, solvent refining, hydrogen processing, hydrocracking, oligomerization, esterification, and rerefining.

Base oils are classified in the following **five general categories**:

1. Group I base oils

   They are defined to "*contain less than 90 percent saturates and/or greater than 0.03 percent sulphur and have a viscosity index greater than or equal to 80 and less than 120*" [2.2].

   They represent the least refined group of oils manufactured by solvent extraction of crude oil distillate, a comparably simple method, resulting in a relatively low price but also lower quality. Hence, group I base oils are generally used in less demanding applications [2.4, 2.5].

2. Group II base oils

   Appendix E defines them to "*contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulphur and have a viscosity index greater than or equal to 80 and less than 120*" [2.2].

   Group II base oils exhibit better performance in some oil parameters, such as volatility, oxidative stability (due to high grade of saturation), and flash/fire point but only limited behaviour regarding certain properties, such as pour point, cold crank viscosity and extreme pressure wear. They are produced by hydro-processing (hydrocracking), a more intensive process than for group I base oils, leading to a higher price but also to a higher quality in comparison with group I. Thus, group II base oils are recommended for more challenging applications and are commonly utilized in engine oils currently available on the market [2.4, 2.5].

3. Group III base oils

   Base oils of group III have to "*contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulphur and have a viscosity index greater than or equal to 120*" [2.2]. They constitute the highest level of oils refined from crude mineral oil, produced by severe hydrocracking processes at higher pressure and heat. Group III base oils are pure and possess elevated performance regarding many oil parameters as well as a highly molecular uniformity and stability. In combination with additives, they are used to formulate high performance lubricants and are sold as synthetic or semi-synthetic products [2.4, 2.5].

4. Group IV base oils

   Appendix E classifies group IV base oils as polyalphaolefines interchangeable without additional qualification besides the manufacturer's specifications [2.2]. They are chemically engineered by oligomerization of alpha-olefins and very common for synthetic base stock.

   Synthetics exhibit highest purity, uniformity and stability, as well as high performance qualities in a wide range of lubricating properties when blended with additive packages suitable for the designated application. Thus, they are utilized in special demanding applications.

5. Group V base oils

   This group of base oils summarizes all base stocks that are not classifiable in group I, II, III, or IV [2.2]. Examples thereof are alkylated naphthalenes, esters, polyalkylene glycols (PAG), silicones, polybutenes, or biolubes.

These compounds are synthetic and are usually characterized by high quality parameters. Often, they are not utilized as base stocks themselves but as additives in other base oils for property improvement and as base stocks for additives.

Table 1 gives a summary of the requirements of the five base oil categories.

Table 1: Overview of the API base oil categories definitions

Base oil category	Manufacturing method	Sulfur content [%]	Saturates content [%]	Viscosity Index [-]
Group I	solvent refined	> 0.03	< 90	80 to 120
Group II	hydrotreated	≤ 0.03	≥ 90	80 to 120
Group III	hydrocracked	≤ 0.03	≥ 90	≥ 120
Group IV	synthetic	Polyalphaolefines		
Group V	diverse	all others not included in I, II, III, or IV		

2.2.2. Additives

Generally, additives are chemical compounds, which provide additional properties to base oils (e.g. detergents, dispersants, extreme pressure additives, viscosity improver) or which improve already existing base oil properties (e.g. antioxidants, antifoam additives). Modern engine oils contain up to 25 % of various additives, which does not mean, that the total amount of additives consists of active ingredient. Additives are usually sold as solutions in oil so that the active compound may be only a fractional amount of the total additive.

Furthermore, it has to be pointed out, that most chemical compounds have more than one effect in a lubricant. Well known examples therefore are the combinations of viscosity modification and pour point depression, detergency with antioxidant behaviour, antiwear with antioxidant activity, and dispersancy with viscosity modification [2.1, 2.6].

In the next subchapters, the most relevant additive types applied in engine oils are discussed in detail according to their main field of application.

2.2.2.1. Antioxidants

Antioxidants are one of the most important additives appending to engine oils. When in contact with oxygen from air at elevated temperatures or at light exposure, oils tend to oxidize, mainly to form acids (detailed mechanism see section 4.1) and polymers which subsequently produce sludge. By the addition of antioxidants, these processes should be reduced or avoided completely.

Antioxidants are divided in **two groups** according to their mechanism of action [2.1, 2.7]:

1. Primary antioxidants

   These are active compounds, which block the first step of the oxidation mechanism, the formation of radicals. They serve as H radical donors as well as peroxide scavengers. The two chemical main types of primary antioxidants to be applied in engine oils are sterically hindered phenolic and aromatic amines.

2. Secondary antioxidants

   On the contrary, secondary antioxidants react almost stoichiometrically with oxygen or with hydroperoxides and are decomposed by oxidation. After the complete consumption of the compound, oil oxidation processes commence without hindrance.

2.2.2.2. Detergents

Detergents are chemical compounds which primarily have the function to prevent or minimize the formation of deposits on hot engine parts, e.g. piston or piston rings. They also have the ability to disperse soot or other contaminations in the oil. However, detergents do not serve to clean already existing deposits.

Currently, the commonly applied detergents in engine oils are phenolates, sulfonates, and salicylates, whereupon usually bivalent metal atoms, mostly calcium, sometimes also magnesium or barium, serve as counter ion. In that manner, the secondary valence may be linked to inorganic radicals such as hydroxide or carbonate. The bonding between organic moiety and metal atoms is largely ionic, subsequently an organic moiety is not permanently associated to a defined metal ion, but can exchange with others. Hence in practice, it is not possible to specify a particular chemical structure for detergents. However, they are more likely defined according to their ratios of the metal to organic and inorganic moieties on an overall basis.

Figure 6 shows exemplarily the scheme of a detergent micelle with a calcium carbonate core (right side) as well as the adsorption of detergent molecules on the metal surface of engine parts (left side).

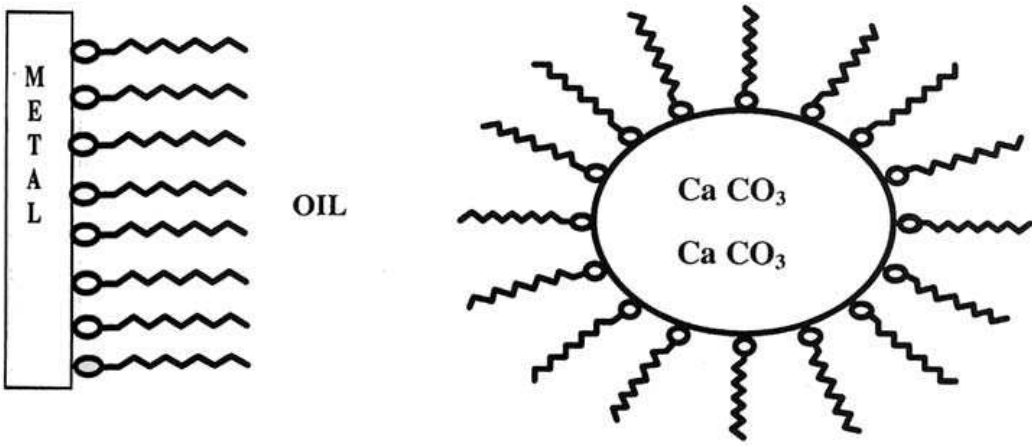

Figure 6: Idealized representation of detergent molecules on the metal surface (left) and as micelle with a calcium carbonate core (right) [2.8]

Many detergents contain a so-called “alkaline or base reserve”, which means, they exhibit an excess alkali or base (mainly carbonate), which is used to neutralize acidic components formed during combustion or by oil degradation. This base reserve is represented by the Total Base Number (TBN), an important parameter for engine oils (for details see section 3.1.2) [2.1].

2.2.2.3. Dispersants

Dispersants act as mild detergents and were originally developed for the dispersion of water in gasoline engine oils. The main intent of dispersants is to interfere in the agglomeration of contamination or degradation particles by associating with them and hence suppressing the formation of oil insoluble deposits.

The larger the particles – soot or oil degradation products (resin) – become, the more likely they are precipitated. Growth of these insolubles happens due to dipolar forces (between resin particles) or by absorption of polar contaminations such as water or oxygen components resulting in adhesion (in soot). Also interaction between soot and adhesive resin molecules occurs, which is shown in A) and B) in Figure 7. In order to avoid such agglomeration, dispersant particles associate with single soot or resin particles, hence hindering them to combine to larger particles (see C) and D) in Figure 7).

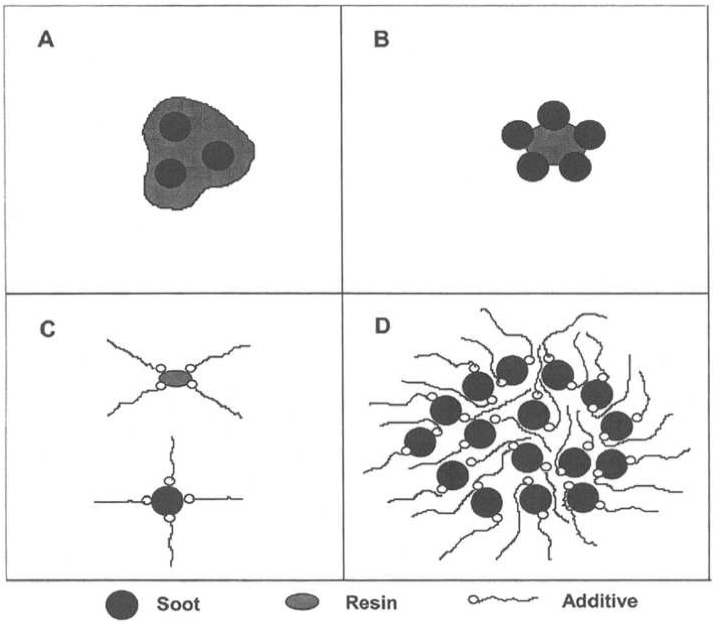

Figure 7: Mechanism of interaction between soot, resin, and dispersants [2.8]

A) Soot particles caught in adhesive degradation products (resin)

B) Degradation particle (resin) agglomerated in soot particles

C) Association of dispersant molecules with soot and resin

D) Avoidance of agglomeration due to steric hindrance

Dispersants are ashless meaning that they do not contain any metal ions and hence do not produce ash upon combustion. Generally, a dispersant molecule can be divided into three distinct structures: 1) a polymeric hydrocarbon group, 2) a polar group usually nitrogen- or oxygen-derived and 3) a connecting group between 1) and 2), e.g. succinimide, phenol, or phosphonate. The graphic representation of a dispersant molecule is given in Figure 8 Typical representatives of this additive group frequently used in engine oils are succinimides, mostly polyisobutylene succinimides.

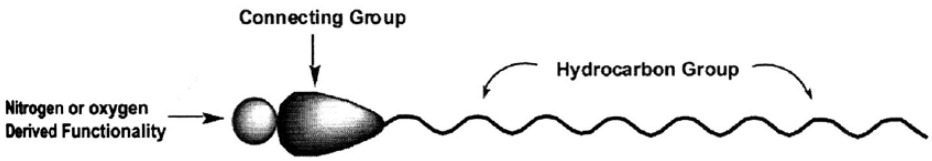

Figure 8: Schematic representation of a dispersant molecule [2.8]

Besides their main function to disperse contaminations in the oil, they support the thermal and oxidative stability as well as contribute to the viscosity characteristics of an oil [2.1, 2.8].

2.2.2.4. Antiwear and extreme pressure additives

In the boundary lubrication regime, asperities of the machine interfaces start to have contact to each other. Seizure, scuffing and severe surface damage are the consequences. Antiwear (AW) and extreme-pressure (EP) additives are applied in lubricating oils in order to avoid direct metal-metal contact by formation of tribolayers.

The distinction between AW and EP additives and consequently their classification is often not clear. They can be ranged as AW additives in the one application and as EP additives in other implementations. In general, antiwear additives are assigned to form surface films, mono- or multilayer, under normal operating conditions, hence eliminating the direct contact of sliding surfaces and reducing the rate of continuous moderate wear. On the contrary, EP additives are designed to react rapidly with the respective surfaces under conditions of high strain and in cases of significant degree of surface contact so that other surface-active additives are not able to form protective films anymore.

Nowadays, zinc dialkyldithiophosphate (ZDDP) is the most frequently used antiwear additive in engine oils, transmission fluids, and hydraulic oils. Thereby, ZDDP is rather a class of additives than a component with particular structure. A representative structure of ZDDP is shown in Figure 9.

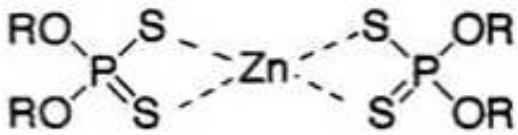

Figure 9: Representative structure of ZDDP [2.8]

Nonetheless, problems arose concerning the characteristic of phosphorus in acting as automotive catalyst poison and the environmental contamination by zinc, which led to the development of metal- or phosphorus-free compounds to replace ZDDP with ashless additives. Examples are the following groups of additives [2.1, 2.8]:

- Sulfur additives (sulfurized olefins, esters, and oils)
- Phosphorus additives (phosphate esters, phosphites, dialkyl alkyl phosphonates, acid phosphates)
- Sulfur-phosphorus additives (ashless dithiophosphates, ashless phosphorothioates and thiophosphates)
- Sulfur-nitrogen additives (dithiocarbamates, dimercaptothiadiazole and mercapto-benzothiazole additives),

- Phosphorus-nitrogen additives (amine phosphates, amine thiophosphates and dithiophosphates)
- Nitrogen additives (dicyano compounds, polymide-amine salts of styrene-maleic anhydride copolymers, products of nitrogen heterocycles such as benzotriazole and tolytriazole with amines or carboxylic acids)
- Halogen additives (perfluorinated compounds, chlorinated paraffins, chlorinated fatty acids and their derivates, but chlorine additives are no option for modern lubricants due to environmental issues)

2.2.2.5. Viscosity modifiers

Viscosity modifiers reduce the viscosity-temperature dependence of the base oil in lubricants and were established for the formulation of multigrade lubricants in the 1960s. Multigrade oils enable engines to start at low temperatures and provide additionally a sufficiently high viscosity at elevated temperatures to avoid engine wear. They are oil-soluble polymers that thicken the oil at high temperatures due to a voluminous conformation and hence interactions within the molecules while minimizing the thickening effect at low temperatures, when the polymers appear as small-shaped spheres without exchanges with each other (see Figure 10).

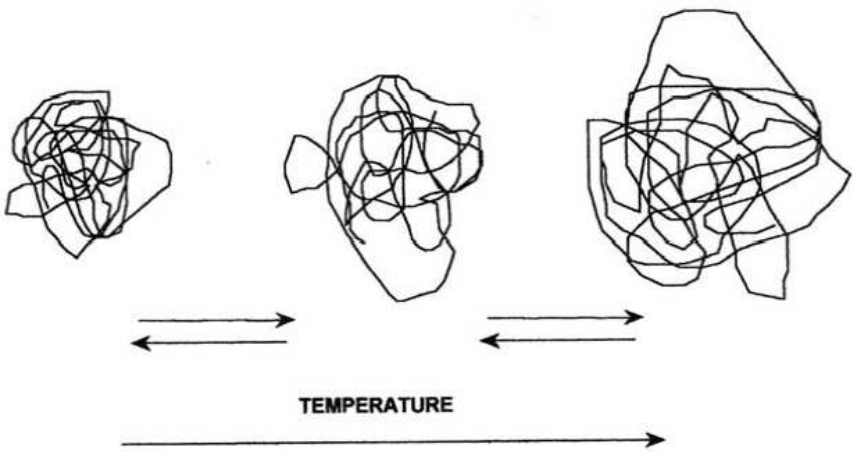

Figure 10: Effect of viscosity modifiers at lower temperatures (left) and at higher temperatures (right) [2.8]

Table 2 gives an overview of commonly applied viscosity modifiers with their respective chemical polymer structure.

Table 2: Overview of viscosity modifiers [2.8]

Viscosity modifier name	Abbreviation	Polymer structure
Olefin copolymer Poly(ethylene/propylene) [may contain diene termonomer]	OCP	Linear copolymer, can contain long-chain branching
Polyalkylmethacrylate	PMA	Linear copolymer
Hydrogenated radial polyisoprene, can contain styrene as comonomer	HRI	Star polymer
Hydrogenated styrene-isoprene	HIS	Linear A–B block copolymer
Hydrogenated styrene-butadiene	HSB	Linear tapered block copolymer
Polyisobutylene	PIB	Linear homopolymer
Styrene-ester, alternating copolymer of styrene and alkylmaleate	SE	Linear copolymer

2.2.2.6. Pour point depressants

This type of additive is brought in the oil to lower the temperature at which it coagulates, namely the pour point, the lowest temperature at which the oil is still capable of flowing (see chapter 3.1.6). At low temperatures, it comes to a separation of wax, crystallizing in large plates, forming spacious networks, thus hindering or in the worst case blocking the oil flow.

Pour point depressants are polymers designed to eliminate the formation of wax crystals by preventing the molecules to fuse together. Hence, an improvement of the low temperature behaviour of the oil as well as an improvement of the low-temperature pumping viscosity is achieved

Commonly applied chemical compounds are polyalkylmethacrylates, styrene ester polymers, alkylated naphthalenes, ethylene vinyl acetate copolymers, and polyfumarates with a typical treat rate of less than 0.5 % [2.1, 2.8-2.10].

2.2.2.7. Foam inhibitors

Foam build-up or the entrainment of gases reduce the effectiveness of lubricants, leading to lowered oil pressure as well as to engine damage. Entrained air may cause cavitation of the oil film or improper actuation of hydraulic unit injectors. Hence, these phenomena have to be eliminated during engine operation, especially in lubricants with a high number of different additives as the stability of built foams rises with the quantity of additives.

Chemical structures commonly used as foam inhibitors are dimethylsiloxane polymers, alkylmethacrylate copolymers, and alkylacrylate copolymers. They possess only borderline

solubility in the oil and must occur in fine dispersion for an effective function. Their mechanism of action is based on the reduction of the surface tension at the interface to air bubbles, making them burst easily [2.8].

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3. Analytical methods for engine oils

A large number of analytical procedures are available and standardised for the characterisation and classification of oils. For each oil type, a typical analyses portfolio exists to specify the most important properties of the respective oil according to its application.

In this chapter, main focus is laid on the analytical methods commonly applied for engine oils ranging from fresh oil characterisation to oil parameters that usually change by specific alteration mechanisms.

3.1. Fresh oil parameters

3.1.1. Viscosity and viscosity index

Viscosity is one of the most important physico-chemical oil parameters. It is a measure for the flowability of an oil sample under various stress conditions, in particular temperature, shear and pressure. Viscosity or rheological properties, respectively, are responsible for the formation of a hydrodynamic lubricating film.

It has to be differentiated between dynamic and kinematic viscosity: traditionally, the **dynamic viscosity** is defined as one poise to be "*the force in dynes to move 1 cm² of surface in the fluid past a parallel 1 cm² at a distance of 1 cm within the fluid, and at a speed of 1 cm/second*" given in the more convenient unit centipoise (cP) which is also expressed by 1 milliPascal second in SI units (1 cP = 1 mPa × s). The **kinematic viscosity** is determined by allowing a fluid to fall under its own weight, resulting in the unit centistokes (cSt), which can be expressed in SI units as mm²/second. It is equal to the dynamic viscosity divided by the density of the respective fluid at the given temperature [3.1].

The methods for measurement of both viscosity types possess high diversity and are defined in numerous standards. The kinematic viscosity is determined by **capillary viscometers** by the detection of the time a fluid volume needs to flow between two defined marks. This fundamental method is applied under varying test conditions in the standards DIN 53019-1 [3.2], DIN EN ISO 3104 (Ubbelohde viscometer) [3.3], DIN 51562-1 (Ubbelohde viscometer) [3.4], DIN 51366 (Cannon-Fenske viscometer) [3.5], ASTM D 445 [3.6], ASTM D 7279 (Houillon visometer) [3.7], and ASTM D 4624 (high-temperature-high-shear viscometer, but withdrawn 2004) [3.8].

Rotational viscometers measure the dynamic viscosity typically by the assessment of the torque required to rotate a body immersed in the oil sample at a given speed or the speed resulting from a given torque, utilizing the viscous resistance affecting the movement of the

rotor. This measuring principle can be found in a large number of standards, the testing conditions of which often refer to those in the respective oil applications, i.e. ASTM D 7042 (Stabinger viscometer) [3.9], ASTM D 2983 [3.10] and accordingly DIN 51398 (Brookfield viscometer) [3.11], ASTM D 5133 (Brookfield viscometer scanning technique) [3.12], ASTM D 5293 [3.13] and accordingly DIN 51377 (cold cranking simulator, CCS) [3.14], ASTM D 4684 (mini rotary viscometer) [3.15], ASTM D 4683 (tapered bearing simulator) [3.16], and ASTM D 4741 (Ravenfield viscometer for high-temperature high-shear testing) [3.17].

Standard J300 of the Society of Automotive Engineers (SAE) [3.18] "*defines the limits for a classification of engine lubricating oils in rheological terms only*". In Table 3, a summary of the viscosity grades relevant for engine oils regarding J300 is given. In doing so, low temperature viscosities are given as CCS viscosity according to [3.13] and as pumping viscosity according to [3.15]. High temperature viscosities are measured as kinematic viscosity at 100 °C according to [3.6] as well as dynamic viscosity at 150°C and at high shear rate according to [3.16] or [3.17].

Table 3: Overview of viscosity grades relevant to engine oils according to J300 [3.19]

SAE viscosity grade	Low temperature viscosities		High temperature viscosities		
	CCS viscosity [mPa*s] max at °C	Pumping viscosity [mPa*s] max at °C	Kinematic viscosity [mm²/s] at 100°C min	Kinematic viscosity [mm²/s] at 100°C max	High shear rate viscosity [mPa*s] at 150°C and 10^6 s^{-1} min
0W	6 200 at -35	60 000 at -40	3.8	---	---
5W	6 600 at -30	60 000 at -35	3.8	---	---
10W	7 000 at -25	60 000 at -30	4.1	---	---
15W	7 000 at -20	60 000 at -25	5.6	---	---
20W	9 500 at -15	60 000 at -20	5.6	---	---
25W	13 000 at -10	60 000 at -15	9.3	---	---
20	---	---	5.6	< 9.3	2.6
30	---	---	9.3	< 12.5	2.9
40	---	---	12.5	< 16.3	2.9 (0W, 5W, 10W)
40	---	---	12.5	< 16.3	3.7 (15W, 20W, 25W, single grade)
50	---	---	16.3	< 21.9	3.7
60	---	---	21.9	< 26.1	3.7

The **viscosity index** (VI) is defined by the standards DIN ISO 2909 [3.20] and accordingly in ASTM D 2270 [3.21] and depicts a value, which describes the change in kinematic viscosity of a lubricating oil due to change in temperature. Higher values of VI result in a lower dependency of viscosity on temperature. Exemplarily, when comparing two oils with the

same viscosity at 100°C but different VI, the oil with higher VI shows a lower impact of the ambient temperature on viscosity, i.e. this oil has a lower viscosity at ambient conditions.
Table 4 gives an overview of various lubricant base oils with their respective VI. Obviously, mineral oils possess the lowest VI whereas synthetic base stocks such as PAO, esters, polyalkylene glycol, or perfluoroalkyl ether exhibit significantly higher VI, e.g. silicon oils which have a 4 to 5 times higher VI than mineral oils.

Table 4: Examples of lubricant base stocks and their respective VI [3.19]

Lubricant	**VI**
Mineral oil	~ 100
PAO	~ 170
Synthetic ester	~ 180
Polyalkylene glycol	~ 190
Perfluoroalkyl ether	~ 300
Silicon oil	~ 430

For demanding applications, VI is increased by the addition of viscosity modifiers, see section 2.2.2.5. By this means, single grade engine oils with low VI (100 and lower) and hence a high temperature dependency of their viscosity, are transformed to so-called multi-grade oils with higher VI (higher than 100). The viscosity of these oils shows only marginal dependency on the ambient temperature, thus ensuring a sufficiently fluidic lubricant at lower temperatures as well as an adequately higher viscosity at applications provoking high temperatures.
According to [3.20], the VI is calculated from the kinematic viscosities at 40 and 100 C measured by the method described in [3.3]. In doing so, two different calculation formulas are defined depending on whether the VI is lower (variant A) or higher (variant B) than 100.

Variant A calculates the VI by using the equation

$$VI = (L - U) / (L - H) \times 100$$

whereupon L stands for the kinematic viscosity at 40 °C, given in (mm²/s) of a petroleum product which exhibits a VI of 0 and the same viscosity at 100 C as the testing substance. Furthermore, H depicts the kinematic viscosity at 40 °C, given in (mm²/s) of a petroleum product which exhibits a VI of 100 and the same viscosity at 100 C as the testing substance.

If the kinematic viscosity of the testing substance at 100 °C lies between 2 and 70 mm²/s, the respective values for L and H are listed in [3.20]. If it is higher than 70 mm²/s, L and H are calculated as follows:

$$L = 0.8353 \times Y^2 + 14.67 \times Y - 216$$
$$H = 0.1684 \times Y^2 + 11.85 \times Y - 97$$

whereupon Y is the kinematic viscosity at 100 °C given in (mm²/s) of the testing substance.

Variant B for liquids with a VI of 100 or higher prescribes the determination of the VI by following equation

$$VI = [(10^n - 1) / 0.00715] + 100$$

n is calculated as follows

$$n = (\log_{10}H - \log_{10}U) / \log_{10}Y$$

whereupon U is the kinematic viscosity at 40 °C given in (mm²/s) of the testing substance and Y depicts the kinematic viscosity at 100 °C given in (mm²/s) of the testing substance. Values for H are determined according to the same procedure as described for H in variant A.

3.1.2. Total Base Number (TBN)

In standard DIN ISO 3771 [3.22], the total base number is defined to be the amount of perchloric acid in equivalent milligrams of potassium, necessary to neutralize all basic components in 1 g of oil sample under the described titration conditions. Thus, TBN is a measure for the alkaline (base) reserve in an oil typically brought in by basic additives (see chapter 2.2.2). Alternatively, TBN can also be given in milli-equivalent hydroxide per gram but this unit is not in practical use.

In [3.22], a procedure is described, where an oil sample aliquot is dissolved in a mixture of anhydrous chlorobenzene and glacial acetic acid and titrated with a standard solution of perchloric acid in glacial acetic acid with the help of a potentiometric measuring device. A glass electrode as indicator electrode and a calomel reference electrode are applied, respectively. By plotting the measured values for the potential versus the respective volumes of titration liquid, the end point of titration is determined as the last inflexion point of the

gained titration curve. This standard is intended to be replaced by DIN 51639-1 [3.23], which proposes a very similar procedure but where the oil sample is dissolved in a mixture of toluene, acetone, and glacial acetic acid and the titration is detected by a single-rod measuring cell and is alternatively described in ASTM D 2896 [3.24].

A different method for the determination of the base number is given in DIN ISO 6618 [3.25], where a colour-indication titration with hydrochloric acid is described. The oil sample is dissolved in a mixture of toluene and isopropanol with a small amount of water and afterwards titrated with an alcoholic standard solution of hydrochloric acid. The end point is determined by the colour change of the indicator solution p-naphtholbenzein. An equivalent procedure is described in ASTM D 974 [3.26].

3.1.3. Neutralization Number (NN) or Acid Number (AN)

The content of acid components in an oil sample can be expressed by two oil parameters: the neutralization number (NN) or the acid number (AN).

Standard DIN 51558-1 [3.27] defines three types of NN:

1. NN (acidic), also called total acid number (TAN), as the amount of base expressed in mg KOH necessary to neutralize all acidic components in 1 g of oil sample
2. NN (alkaline), also called strong base number, as the amount of acid expressed in mg KOH necessary to neutralize all alkaline components in 1 g of oil sample
3. NN (water soluble acids), also called strong acid number as the amount of base expressed in mg KOH necessary to neutralize all water soluble acidic components in 1 g of oil sample

For the determination of 1) and 2), the sample is dissolved in a mixture of toluene and isopropanol with a defined amount of water and titrated with alcoholic KOH or alcoholic HCl until the end point, which is indicated by the colour change of p-naphtholbenzein. In order to determine 3), a sample aliquot is extracted with hot water followed by a titration of the water phase with KOH with the application of methyl orange as indicator. Alternatively to the procedure described in 3), a method for the measurement of the NN – also called the strong acid number – is described in [3.26].

Standard DIN EN 12634 [3.28] defines the AN to be the amount of base in mg KOH per g oil necessary to titrate the acidic components in a sample aliquot by potentiometric means. In doing so, the oil sample is dissolved in a mixture of dimethylsulfoxide, isopropanol, and toluene (1:8:7) and titrated with an alcoholic tetramethylammonium hydroxide solution. The titration is detected potentiometrically by a glass electrode and a reference electrode. The end point is the last inflexion point of the titration curve. An equivalent procedure for the

determination of the AN is described in ASTM D 664 [3.29], whereupon the sample is dissolved in a titration solvent consisting of water, anhydrous isopropanol, and toluene followed by a titration with alcoholic potassium hydroxide.

3.1.4. Saponification Number (SN)

The saponification number is a measure for the content of saponifiable components in lubricating oils and therefore displays the content of free and bound acid of an oil sample. DIN 51559-1 [3.30] (based on the standard ASTM D 94-07 [3.31]) defines the SN as the quantity of base expressed in mg KOH consumed under defined conditions. The sample is dissolved in a mixture of toluene and isopropanol and afterwards heated with 25 mL of KOH dissolved in ethanol. Subsequently, a titration is carried out with HCl and phenolphthalein as colour indicator to determine the amount of residual (unreacted) KOH. Then, SN is calculated from the amount of consumed KOH upon saponification.

3.1.5. Flash point

The flash point is the criterion which defines the inflammablility of an oil. Oils are divided in different hazard categories by their flash point. Furthermore, this value can give information of contaminations in the oil, e.g. fuel dilution causes a significant decrease of flash point.

The measurement of flash point can be carried out with a closed or open cup:

Using **closed cup**, standard DIN EN ISO 3679 [3.32] defines the flash point to be the lowest temperature (corrected to the air pressure of 101.3 kPa) at which – under defined testing conditions – the vapour phase of the oil sample is ignited immediately by the ignition source and thus, a flame spreads over the surface of the liquid sample. For this method, the oil sample is filled in a closed cup, which is heated to the estimated flash point of the sample. After a defined duration, the ignition source is immersed in the vapour phase and it has to be observed whether an ignition had taken place or not. These ignition tests are repeated at different temperatures with fresh aliquots of the sample until the flash point is measured with the prescribed accuracy.

A similar procedure, the Pensky-Martens method, is described in DIN EN ISO 2719 [3.33]. Thereby, the sample is filled in a closed cup of a Pensky-Martens measuring device and heated under stirring with a constant temperature increase. The ignition source is lowered in regular intervals through an opening in the cover, whereupon the stirring is interrupted. The flash point is given as the lowest temperature, at which the vapour phase above the sample can be ignited and the flame is spreading over its surface.

Alternative methods are described in the standards ASTM D 93 [3.34], ASTM D 3278 [3.35], and ASTM D 7236 [3.36].

An open **cup method** determining the flash point is the measurement according to the Cleveland open cup method described in DIN EN ISO 2592 [3.37], where the sample is heated in an open device, first very fast and with minor heating rate near the flash point. The ignition source is lowered in constant intervals over the sample. The flash point at ambient conditions is given as the lowest temperature at which the vapour phase is ignited. In order to determine the fire point, the same sample is again heated until the ignition source is able to ignite the vapour phase over the sample and the flame continues for at least 5 s. Both, the flash point and the fire point have to be corrected to an air pressure of 101.3 kPa.

An equivalent method for the determination of the flash point by the Cleveland open cup tester is described in ASTM D 92 [3.38].

3.1.6. Pour point

Deep temperatures are problematic for oil lubricated systems, especially in winter time, as it is possible that the oil thickens or even solidifies. Therefore, an important parameter for the application of oils in engines is the pour point, which is defined by DIN EN ISO 3016 [3.39] to be the lowest temperature at which the oil barely flows when it is cooled down under prescribed conditions. This standard describes a procedure of cooling down the sample, and at constant time intervals, the sample is taken out of the cooling device and tested whether it is pourable or not. If not, the cooling procedure it continued to even lower temperatures.

Besides this standard, ASTM D 97 [3.40] describes an equivalent procedure to determine the pour point of an oil sample.

3.2. Oil alteration parameters

In order to guarantee possibly long operating times, i.e. safe machine operation without events of damage, it is necessary to know the condition of used lubricating oil. This is the aim of **used oil analysis** or **oil condition monitoring** which makes use of a multitude of analytical tools

1. to compare data from used lubricants with the respective fresh oil data to determine and measure changes in oil properties or
2. to introduce new parameters for the characterization of a lubricant in service.

For each oil type, a tailor-made assortment of analyses adapted to the respective specifications is defined that an oil has to cope with the requirements in the real field. Thus, data especially important for the respective range of application can be provided.
The focus in the following sections is laid on the used oil analysis of engine oils.

3.2.1. Appearance (colour and transparency) and odour

The first and most evident used oil parameter is the visual appearance of an oil sample that has to be reported. Changes in oil properties like colour or transparency provide important information about the oil condition such as state of degradation or possible contamination by liquid or solid compounds. For example, it is possible to identify higher water contents in the oil by turbidity, hence leading to the conclusion of damage in the cooling system of an engine. Furthermore, the presence of wear particles in the lubricating oil indicates difficulties in a proper motor operation.
In addition, it is easily possible to draw conclusions about the condition of an oil sample from its odour. This parameter has to be included in an analysis report as well. Thus, it has to be distinguished whether the odour is typical for a special oil sample or not. Untypical odours may range from penetrative, acidic to foul-smelling. By this way, contamination with various substances such as fuel or cooling liquid can be noticed [3.41].

3.2.2. Change in viscosity behaviour

During operation of a lubricating oil, mechanical stresses and chemical reactions occur leading to changes in the viscosity behaviour. In that manner, two processes compete against each other, i.e.

1. a viscosity increase by
   - the development of oxidation products of the base oil
   - the accumulation of suspended wear particles and other insoluble matter
   - increase of dissolved resins from incomplete combustion
2. a viscosity decrease by
   - dilution with low viscous components, e.g. fuel
   - the depletion of viscosity modifier molecules due to shear stress

For a safe machinery operation, the proper viscosity behaviour of the in-service lubricant has to be guaranteed. Out of this reason, the measurement of viscosity according to one ore more methods described in chapter 3.1.1 is indispensable for a comprehensive oil condition monitoring.

3.2.3. Fourier Transform - Infrared spectroscopy (FT-IR)

Analysis by Fourier Transform Infrared spectroscopy is one of the most important and significant tools for the characterisation of used oils applied for decades. By this means, oil spectra can be interpreted for contaminations such as water, glycol, or soot as well as alteration procedures, i.e. due to additive depletion, oxidation, nitration, and sulfation [3.41].

The interaction of the oil sample with infrared radiation, typically in the area of 4000 to 650 cm^{-1}, is monitored. By excitation of defined vibrations in the molecules, energy is absorbed hence producing an absorption spectrum which is typical for the investigated molecule. Thus, the availability of characteristic spectra for each substance enables the identification of the respective substance in complex mixtures such as lubricants.

Commonly, an interferogram measured by a Michelson interferometer is transformed by Fourier Transformation to an amplitude vs. wave number spectrum. Thereby, the Lambert-Beer law specifies the ratio between the intensity of light before the interaction (I_0 given in (W/m²)) and the intensity of light after the interaction (I given in (W/m²)) [3.42- 3.44], i.e.

for transmission: $T = I / I_0 = 10^{-c \times d \times e}$,

for absorption: $A = c \times d \times e$, and the

relationship between absorption and transmission: $A = -\lg T$

whereupon T stands for dimensionless transmission, c for concentration given in (mol/L), d for thickness of sample layer in (mm), e for absorption coefficient in (m²/mol), and A for dimensionless absorption.

From these equations it is obvious, that the absorption is proportional to the concentration of the respective component, hence absorption spectra can be utilized for quantitative analysis [3.42].

The general working principles for obtaining FT-IR spectra as well as the apparatus requirements are defined by standard DIN 51451 [3.45].

In ASTM E 2412 [3.43], a standard practice describes the condition monitoring of lubricants by the fast and simple spectroscopic FT-IR method to analyse the operation condition of the machinery by detection of changes in the respective oil. Such changes comprise water up-take, oil oxidation, additive depletion, and others. Condition monitoring for engine oils is usually divided in two parts: 1) monitoring of lubricant degradation and 2) monitoring of external contamination [3.43].

For that matter, two approaches can be distinguished: 1) direct trending where the measured spectrum is directly analysed and 2) spectral subtraction where a difference spectrum between

fresh and used oil is calculated. In the following sections, these methods of calculation are described in detail.

3.2.3.1. Detection of oil degradation by oxidation, nitration, and sulfation

During the usage of lubricating oil, oxidation processes occur due to the impact of oxygen from the air resulting in the built-up of carbonyl-containing degradation products, i.e. esters, aldehydes, ketones, lactones, carboxylic acids, and carboxylate salts. These chemical reactions comprise the main part of oil degradation and are described in detail in section 4.1. Furthermore, more or less strong nitration processes take place especially in engine oils provoked by nitric oxides developed during the combustion and brought in via blow-by gases. Aside from that, sulfation occurs due to the introduction of sulfur from the combustion or from oxidation of sulfur compound from the base oil or additives [3.43, 3.46].

In [3.43], the oil alteration parameter "**oxidation**" is represented by carbonyl formation and measured by spectral subtraction as the maximum peak height between 1800 and 1650 cm^{-1} with the baseline taken at 1950 cm^{-1}, see Figure 11. For ester based synthetic oils, the region of measurement can be shifted to the range between 1710 and 1660 cm^{-1} resulting in an avoidance of the large carbonyl band provoked by the ester group.

For the evaluation of the **nitration**, a similar approach is applied by determination of the extinction at a wavelength of 1630 cm^{-1} with baseline endpoints at 1645 cm^{-1} and 1615 cm^{-1}, see also Figure 11.

Both parameters, oxidation and nitration, are given in absorbance per centimetre and therefore the extinction values have to be converted to a nominal cuvette layer thickness of 1 cm. The initial value of the fresh oil is always 0 due to the subtraction procedure.

A similar approach for the detection of oxidation and nitration products developed by oil degradation is presented in DIN 51453 [3.46]. Therein, the extinction is determined at the wavelength of 1710 cm^{-1} with baseline endpoints at 1970 cm^{-1} and 580 cm^{-1}. Similarly, the nitration is determined by the extinction measured at a wavelength of 1630 cm^{-1} with baseline endpoints at 1645 cm^{-1} and 1615 cm^{-1}.

Sulfation, the built-up of sulfur oxidation products, is determined according to [3.43] at the broad band in the area around 1150 cm^{-1}, see also Figure 11 which is a combination of sulfate compounds and carboxylates from oxidation products. The baseline point is set at 1950cm^{-1}.

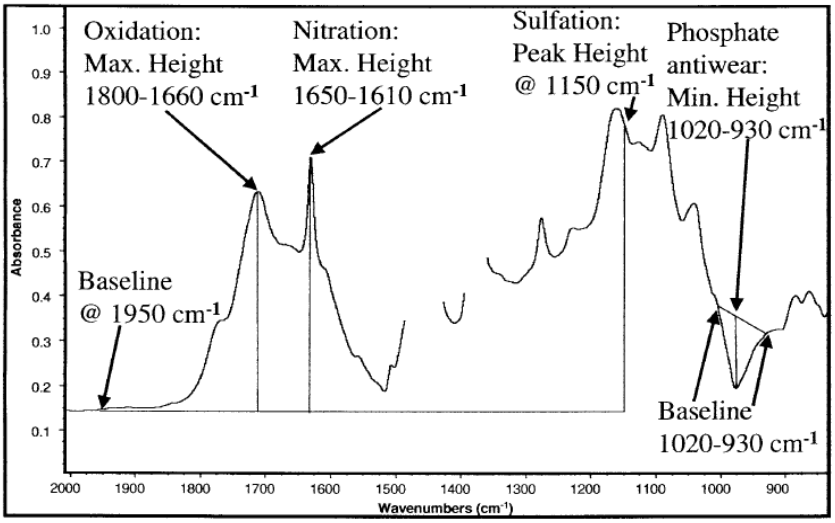

Figure 11: Regions for the evaluation of oxidation, nitration, sulfation, and phosphate antiwear additive

(note: cleared regions between ~ 1480 and 1350 cm^{-1} are areas of total absorbance) [3.43]

3.2.3.2. Detection of contamination built-up by water and soot

Water exhibits two characteristic absorption areas in FT-IR, i.e. at 3400 cm^{-1} and at 1640 cm^{-1}, enabling the detection down to 0.05 to 0.1 wt% [3.43].

According to [3.43], water contamination in lubricating oil is monitored by integration of the absorbance area of the hydrogen-bonded OH stretch region between 3500 and 3150 cm^{-1} carried out by direct trending. It has to be paid attention to high soot levels around 10 wt% as they can lead to interferences with the water determination. Water content can also be detected by spectral subtraction using a baseline at 3700 cm^{-1} measuring the peak height at 3428 cm^{-1}. Alternatively, a two-point baseline from 3740 to 3120 cm^{-1} for the evaluation of the water maximum can be utilized.

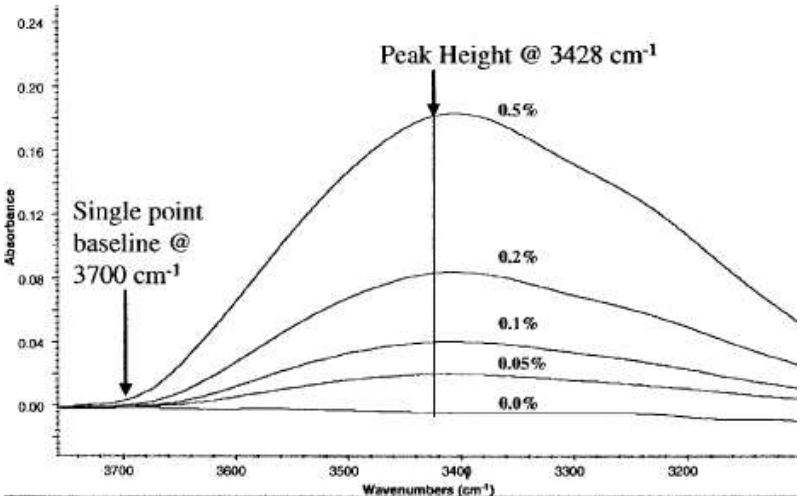

Figure 12: Region for the evaluation of water by spectral subtraction [3.43]

Interferences occur at the presence of compounds containing hydroxyl groups, e.g. ethylene glycol. In such cases, the water content cannot be reliably quantified.

During engine operation, **soot** from incomplete combustion is brought in the oil, especially in diesel engines. DIN 51452 [3.47] describes a method to determine the soot content of used diesel engine oils in percent per weight, which gives information about the remaining detergency of the respective sample.

Soot absorbs infrared radiation depending on the wave number so that higher wave numbers result in higher absorption. Out of this reason, the determination of soot should be carried out at the lowest wave numbers possible. Thereby, the spectral internal transmittance τ is determined at a suitable wave number, where no interferences with hydrocarbons or oil additives emerge. This value is set in correlation with a reference sample, typically the respective fresh oil and hence the soot content is calculated as weight percent w(R) by the following equation:

$$w(\mathrm{R}) = \mathrm{F} \times 1 / d \times (10000 / v)^{0.892} \times lg\ \tau_B/\tau_P \quad [3.47]$$

whereupon d denotes layer thickness of the cuvette in (mm), F is a constant value of 0.048; the slope lg τ_B/τ_P is composed of τ_B as the spectral internal transmittance of the reference oil in (%), and τ_P as the spectral internal transmittance of the sample in (%); and v stands for the wave number in (cm^{-1}). The values for τ_B, τ_P, and v are given at the selected wave number for the measurement.

In addition, [3.43] describes the method of soot content determination by direct trending as the baseline offset at 2000 cm^{-1} as well as by spectral subtraction followed by an assessment of the region at 1950 cm^{-1}.

3.2.3.3. Additive content

Additives exhibit – according to their specific functional groups – characteristic absorption bands in the infrared spectra. By monitoring the existence of different additives and additive groups and in particular their depletion, the condition of the machinery can be observed as well as the remaining useful life of the engine oil can be predicted.

Usually, the evaluation of the content of various additives is performed by in-house methods of the respective company depending on the requirements and application problems. For example, [3.42] gives wide-ranging information about methods utilized for the assessment of additives especially applied in oils for stationary gas engines.

[3.43] proposes a general procedure to determine the content of phosphate antiwear additive depletion, mainly zinc dialkyldithiophosphate, which is monitored as a negative peak in the difference spectra due to the higher content in the spectrum of the fresh oil. For the determination of residual additive content, the peak minimum in the area from 1020 to 930 cm^{-1} with baseline points in the same area is measured (see also Figure 11).

3.2.4. Change in TBN, NN, and AN

By oxidation as well as by the entrainment of blow-by gases from the combustion chamber, acidic compounds are built-up in the oil during operation, which have to be neutralized. This task is covered by the base reserve of an oil brought in as basic additives (see section 2.2.2) the concentration of which is detected via the measurement of the TBN. In the course of the oil degradation, the TBN decreases as a result of neutralization processes. At the time, the base reserve is consumed neutralization is not possible anymore hence leading to a significant increase in NN and AN. In some cases, a NN and AN rise is observed simultaneously to the TBN decrease originating from acidic compounds which do not react with the base reserve.

If the TBN decrease reaches a predefined threshold and if the NN and AN rise to a certain value, respectively, the motor reliability cannot be guaranteed anymore and the engine oil has to be changed. The appropriate thresholds are individually defined by the engine manufacturer or recommended by the oil blender [3.42, 3.48 - 3.50].

3.2.5. Optical emission spectroscopy with inductively coupled plasma (ICP-OES)

The determination of elements primarily informs about two important oil properties: 1) additive composition by detection of the elements from metal organic components, e.g. calcium, sulfur, zinc, phosphorous; and 2) the entry of metal particles due to corrosive or abrasive wear and other contaminations [3.51]. The latter is crucial for the monitoring of in-service oils and hence ICP-OES is another well-established oil alteration monitoring technique.

By this method, the sample is introduced in a plasma and heated to temperatures of 6000 to 10000 K. Thereby, the sample is atomised and the atoms or ions generated are excited and hence brought to a higher energy level. By relaxation from excited state to ground state, radiation is emitted at wavelengths characteristic for the respective element. The content of elements is calculated by comparison with reference solutions of defined element concentrations (calibration). [3.42]

Various standards define the determination of elements in in-service oils. Examples are DIN 51396-1 [3.52] for the evaluation of wear elements Fe, Cu, Pb, Si, Sn, Cr, Al, Ni, and

Mo, DIN 51391-3 [3.53] describing the assessment of the additive elements Ca, Mg, Zn, and Ba, as well as DIN 51399-1 [3.54] combining the detection of elements from additives, wear, and other contaminations. Furthermore, ASTM D 5185 [3.55] deals with the multi-element analysis of lubricating oils in fresh and in-service condition.

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4. Oil alteration

It is generally known, that alteration of lubricants can be basically divided in two main processes: thermal and oxidative [4.1, 4.2].

Note that “alteration” in the context of this research work is understood as any chemical and/or physical changes in lubricant parameterisation regardless of an improving or deteriorating effect on lubricating properties. A common term for “alteration” is “ageing”. Mechanisms going along with lubricant alteration are also called “degradation” or “deterioration” and usually mean loss of lubricant performance.

One kind of oil degradation – with minor priority – is the thermal degradation at elevated temperatures which leads to the cracking of hydrocarbon molecules. Due to developments in engineering, e.g. increase of power density of aggregates, reduced oil volume resulting in a higher load-to-oil ratio, as well as extended oil drain intervals the impact of thermal degradation is growing and accordingly the importance of high thermal stability of lubricating oils.

Besides these reactions, the main degradation processes occurring in oils are oxidation reactions as the lubricant is usually in contact with oxygen. The built-up of oxidation products from base oils and additives is followed – among others – by oil thickening with the formation of sludge and varnish. Consequences thereof are increasing wear of engine parts, insufficient lubrication and low fuel economy. Thus, oxidation processes have a significant impact on the life-time of lubricating oils.

Depending on operating conditions, hydrolysis and shear stress can also contribute to lubricant alteration.

The following subchapter summarizes the mechanism of auto-oxidation.

4.1. Mechanism of oxidation

Mechanism of oxidation is well documented and based on a free-radical chain reaction. It can be divided in four distinct reaction steps [4.1, 4.2]:

4.1.1. Chain initiation

$$R{-}R \xrightarrow{\text{energy}} R^{\bullet} + R^{\bullet}$$

$$RH \xrightarrow{\text{energy}} R^{\bullet} + H^{\bullet}$$

Auto-oxidation starts with the interaction of the hydrocarbon molecules of the oil with energy (heat, UV light, mechanical shear) resulting in the scission of C-C bonds on the one hand or with the hydrogen abstraction on the other hand. Both cases lead to the formation of alkyl radicals. Thereby, the bond strength of the respective C-H bond determines the degree of homolytic cleavage of a C-H bond to form two radicals. The hydrogen atoms with the highest proneness to abstraction are tertiary hydrogens and those alpha-positioned to a carbon-carbon double bond or an aromatic ring.

4.1.2. Chain propagation

$$R^{\bullet} + O_2 \longrightarrow ROO^{\bullet}$$

$$ROO^{\bullet} + RH \longrightarrow ROOH + R^{\bullet}$$

The propagation starts with the very fast formation of an alkyl peroxy radical due to an irreversible reaction of an alkyl radical with oxygen, followed by a slower hydrogen abstraction of an alkyl peroxy radical to form a hydroperoxide and another alkyl radical. Thereby, the alkyl peroxy radical concentration is much higher than the alkyl radical concentration because of the high oxygen concentration available as well the different reaction rates of the two processes.

4.1.3. Chain branching

$$ROOH \longrightarrow RO^{\bullet} + HO^{\bullet}$$

$$RO^{\bullet} + RH \longrightarrow ROH + R^{\bullet}$$

$$HO^{\bullet} + RH \longrightarrow H_2O + R^{\bullet}$$

$$RR'HCO^{\bullet} \longrightarrow RCHO + R'^{\bullet}$$

$$RR'R''CO^{\bullet} \longrightarrow RR'CO + R''^{\bullet}$$

The third step of the auto-oxidation mechanism is chain branching initiated by the cleavage of hydroperoxide into alkoxy as well as hydroxyl radicals. By the reason of its large activation energy, this reaction is only significant at temperatures higher than 150 °C. The produced radicals on their part react with hydrocarbons resulting in the formation of new alkyl radicals, alcohols, and water. Aldehydes and ketones are readily built from secondary and tertiary alkoxy radicals. Further typical oxidation products developed by these processes are carboxylic acids, esters, and CO_2. The compounds generated can provoke the formation of polymeric degradation products and subsequently sludge and varnish.

4.1.4. Chain termination

$$R^{\bullet} + R^{\bullet} \longrightarrow R-R$$

$$R^{\bullet} + ROO^{\bullet} \longrightarrow ROOR$$

$$2\,ROO^{\bullet} \longrightarrow ROOR + O_2$$

Chain termination is accomplished by the combination of radicals. For example, two alkyl radicals recombine to a new hydrocarbon molecule or an alkyl radical reacts with an alkyl peroxy radical resulting in the formation of peroxide. Two alkyl peroxy radicals can react to peroxide with the production of oxygen. Nonetheless, these peroxides are able to break down again in order to form more alkyl peroxy radicals.

4.2. Currently applied standards

4.2.1. General standards

In currently applied standards for the alteration of lubricants, mainly four different procedures are described:

1. thermo-oxidative methods at ambient pressure
2. thermo-oxidative methods under pressure
3. thermo-oxidative methods with catalysts
4. thermo-oxidative methods under pressure and with catalysts

Besides that, special methods are used for particular applications, e.g. testing in the presence of water or testing of insulating oils under electrical stress [4.3] from the year 1981 but withdrawn 1986. But as long as these methods possess only inferior importance or are withdrawn, they are not concerned in this thesis.

The following sub-chapters summarize the four main methods highlighted with relevant standardised methods.

4.2.1.1. Thermo-oxidative methods at ambient pressure

An universal test apparatus, shown in Figure 13, for the evaluation of the oxidative and/or thermal stability of lubricating oils is described in **ASTM D 4871** [4.4]. In this standard, samples of typically 100 mL or 100 g of an arbitrary liquid are kept in glass ware at elevated temperatures of 50 to 375 °C by means of a heated aluminium block. Over glass tubes, the samples can be exposed to various gases at flow rates of 1.5 to 13 L/h adjusted by a gas flow control system. Typical gases used for the alteration of oils are air, oxygen, or nitrogen. The

test apparatus provides the possibility to add water or water vapour as well as insoluble or soluble catalysts.

Figure 13: Universal Oxidation Test Apparatus [4.4]

By regular sampling and analysis of the typical oil alteration parameters, the condition of the oil sample can be monitored throughout the alteration. Additionally, the weight loss of the sample or the formation of sludge can be tracked. Determination of corrosion of metals can be carried out by the evaluation of the appearance, the weight change of metal catalyst specimens, and other methods.

The duration of the test is defined by the operator. On the one hand, the experiment can be terminated after a predefined time period on the other hand it is possible to run the test until the achievement of a predetermined value of a selected oil parameter. A fixed time period is suitable for the performance evaluation of different lubricants, variable alteration durations imply useful information as screening tests.

On the basis of the universal oxidation test apparatus, various standards for the alteration of lubricating oils under thermo-oxidative conditions were developed.

The standard **CEC L-48-A-00** [4.5] is designed to determine the oxidation tendency of automotive transmission (ATF and gear oils) lubricants under defined conditions. The oil is kept at 160 °C (or other specified temperature) for 192 h in an oil bath and with an air flow

bubbling through the sample. Two different apparatus – A and B – are described in [4.5] (see Figure 14).

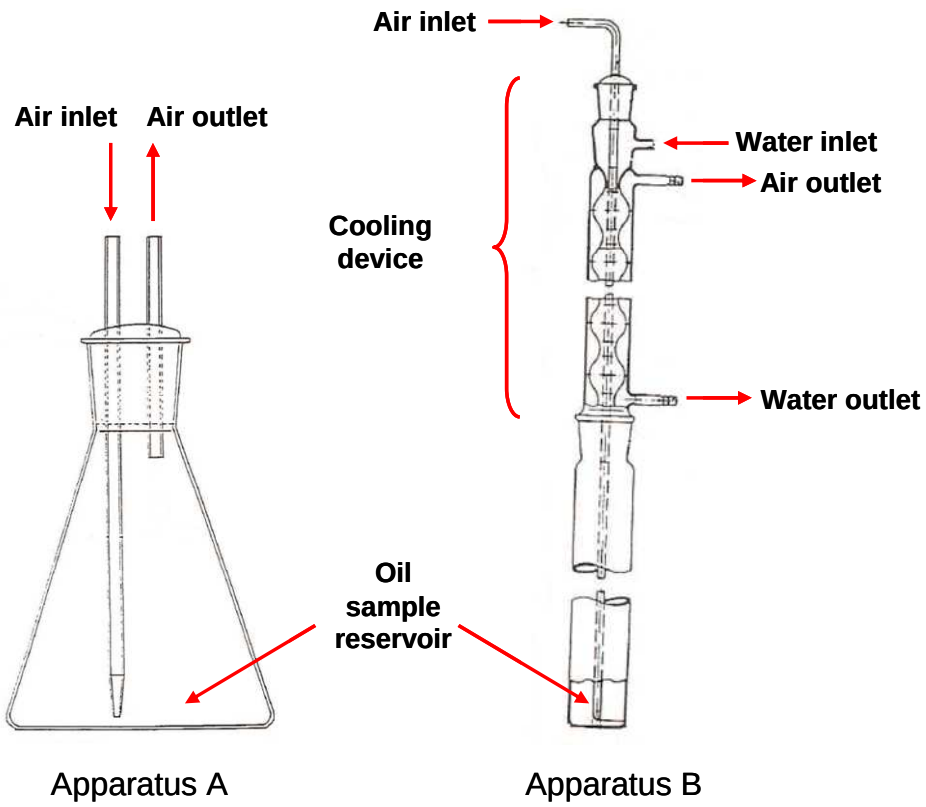

Figure 14: Test apparatus according to CEC L-48-A-00 (modified from [4.5])

Apparatus A is an Erlenmeyer flask that contains 300 mL sample exposed to an air flow of 10 L/h, whereas ***apparatus B*** consists of a flat-bottomed glass tube with an enclosed water cooling device comprising 100 mL of an oil aliquot stressed with an air flow rate of 5 L/h.

The test evaluation covers the mandatory determination of the kinematic viscosity at 40 °C and 100 °C comparing the fresh and altered sample as well as the optional measurement of the changes in acid number.

With apparatus A, the content of heptane insolubles can optionally be determined which corresponds with the quantity of insoluble material in the oil as well as deposits. In addition, FT-IR spectra can be taken, interpreting especially the oxidation peak between 1820 and 1650 cm^{-1} calculating the peak area in this region. Finally, the appearance of oxidized oil sample as well as of the respective flask is reported.

Standard **ASTM D 5763** [4.6] evaluates the oxidation characteristics and the thermal break down of extreme pressure and non-extreme pressure gear oils by exposing 100 g of sample aliquot to a temperature of 120 °C in a heating bath or in a block for 312 h, while dry air is

passed through the oil sample. The air flow is adjusted to 3 L/h, the oxidation cell and the air delivery are made from borosilicate glass.

As test evaluation, the quantification of the total sludge, the changes in viscosity at 100 °C compared to the fresh oil, as well as the evaporation loss during alteration is documented.

ASTM D 2893 [4.7] is developed for extreme-pressure lubrication oils, gear oils or mineral oils. 300 mL oil sample are kept at 95 °C in a heating bath with temperature control for 312 h and subjected to dried air at a flow rate of 10 L/h. The apparatus comprises a glass tube fitted with a slotted cork into which the air flow is passed through via a glass air delivery tube.

The report of the test covers the viscosity at 100 °C in percent increase and the precipitation number, defined as the amount of precipitate formed after mixing 10 mL of oil with 90 mL of ASTM precipitation naphtha and centrifuged.

For oils with an evaporation loss less than 15 mass%, **DIN ISO 6617** [4.8] evaluates the ageing characteristics according to the rise in the Conradson carbon residue, the residue formed by evaporation and thermal degradation of a petroleum product determined under testing conditions described in ISO 6615 [4.9]. 40 mL of sample are held at the elevated temperature of 200 °C for a duration of two periods of each 6 h. Intermediately, the aliquot has to be taken out of the heating bath and stored for 12 to 18 h at ambient temperature. During the ageing periods, 15 L/h of air is bubbled through the oil sample. All tubes and devices are made from borosilicate, heating is achieved via a oil bath with a temperature control and stirrer. The air supply is equipped with glass wool for the reason of filtration.

In the report, following results are noted: evaporation loss, gravimetric evaluation of the absolute weight difference before and after alteration procedure, increase of Conradson carbon residue given as absolute difference before and after alteration procedure.

4.2.1.2. Thermo-oxidative methods under pressure

Thermo-oxidative methods under pressure are based on a different principle, namely the measurement of the consumption of oxygen due to oxidation processes. As evidence, the oxygen pressure in the respective device is monitored.

Among others, **ASTM D 942** [4.10] describes a method to determine the oxidation resistance of greases during storage in an oxygen atmosphere at elevated temperatures. In a pressure vessel, 4 g of grease are stored at 99 °C (210 °F) on sample dishes in a dish holder. The vessel is pressurized with 758 kPa of oxygen. The pressure is detected over the entire alteration duration and recorded at stated intervals.

The standard defines the decrease in oxygen pressure as a measure for the oxidation degree after a distinct time period and determines the net change between pressure drop due to oxidation and pressure rise due to formation of volatile oxidation products.

The method is designed only for the control of grease quality and batch-to-batch uniformity, but is not suitable for the determination of grease stability under dynamic service conditions, stability in long-term storage or stability of grease films in bearings and motor-parts. Moreover, it should not be applied for the comparison of the oxidation stability of different grease types.

Standard **DIN EN 14769** [4.11], designated as accelerated long-term ageing for bitumen and bituminous binders, prescribes a procedure where 50 g of binder sample are placed in a bowl with a 140 mm diameter and a film thickness of 3.2 mm. This device is positioned in a stainless steel pressure ageing vessel (PAV) occupied at the defined pressure of 2.1 MPa and heated to a defined temperature (typically 85, 90, 100 and 110 °C). After the test, the bowls containing the PAV residue are heated in oven for 30 min at 170 °C in order to make binder samples liquid and to proceed with subsequent analyses to determine the impact of the alteration.

The test duration typically constitutes 65 h for the test at 85 °C and 20 h for all other temperatures. It has to be noted, that the chemical changes of bitumen strongly depend on the applied temperature. Thus, possibly low temperatures should be applied to simulate changes a binder in pavement is exposed to during usage.

Standard **ASTM D 6186** [4.12] is targeted at the determination of the oxidation induction period of lubricating oils by pressure differential scanning calorimetry (PDSC). Thus, an oxygen pressure of 3.5 MPa and temperatures between 130 and 210 °C are applied on a small oil sample quantity of 3 mg weighted into an aluminium solid fat index (SFI) sample pan and placed in a test cell. The cell is kept under conditions of stable temperature and stable pressure, until exothermic reactions occur. The duration until this positive heat flow is measured as extrapolated onset time and reported as so-called induction period. It represents an indication of oxidation stability.

Figure 15 shows an exemplary thermal curve as the result of a PDSC experiment with marked tangents and the point of extrapolated onset time at 32.45 min.

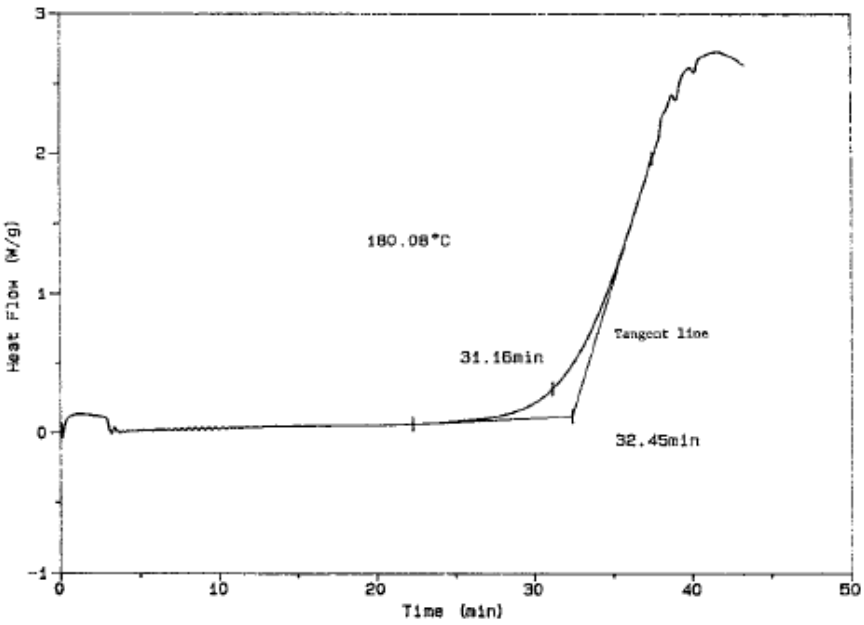

Figure 15: Exemplary thermal curve from PDSC [4.12]

The advantage of this procedure is the use of a very small sample amount. It finds its application in research and development, in quality control issues, and for specification purpose.

4.2.1.3. Thermo-oxidative methods with catalysts

An aggravation of stress compared to conventional thermo-oxidative methods presented in section 4.2.1.1 can be achieved when one or more metals with catalytic impact are implemented in the alteration procedure. On the one hand they are used as ageing accelerators, at the other hand they simulate the contact between oil and machine parts in field application.

A widely known example for these alteration methods is the procedure according to Baader specified in standard **DIN 51554**, a short-term evaluation to predict the performance of mineral oils. The standard is divided in three parts:

Part 1 [4.13] describes the purpose of the method, the sampling and the ageing procedure with the storage of 60 mL of a filtered oil sample at a defined temperature and a defined duration (see part 2 [4.14] and part 3 [4.15]). The periodical immersion of a copper spindle installed on a glass spoon acts as ageing accelerator due to the catalytic effect of the copper and provides input of oxygen as a result of the continuous movement. The number of strokes lies at 25 min^{-1} so that approximately strokes per day of 36000 ± 100 are achieved. It has to be ensured, that the retention time of the copper spindle in the oil is similar to the retention time in the air.

Figure 16 shows the scheme of the alteration device, a glass flask with a fitted water cooling system and the glass spoon extending into the oil sample.

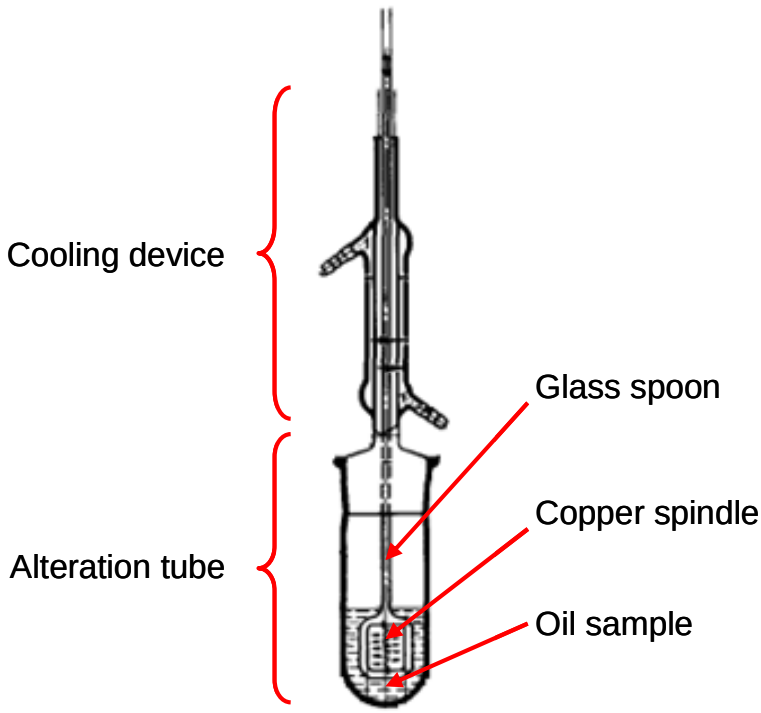

Figure 16: Alteration device according to Baader (modified from [4.13])

Part 2 [4.14] of the Baader method is specially designated for insulating oils. In that manner, two parallel samples are investigated for a duration of 140 h at a temperature of 110 °C. After the test, the visual evaluation regarding changes in the appearance of the oil sample, the glass flask as well as the copper spindle, the saponification number, and the dielectric loss factor at 90 °C are reported. With the second sample, a determination of the amount of sludge developed is performed as chloroform soluble aliquot of the aged sample by gravimetric means.

Part 3 [4.15] of the Baader method especially investigates lubricating oils C, C-L, and C-LP, as well as hydraulic oils H without additives. It prescribes a test duration of 3 days and a temperature of 95 °C. The report consists of a visual evaluation of the change in the appearance of the oil sample and the copper spindle as well as the saponification number.

Standard **DIN 51352 part 2** [4.16] describes an alteration method for mineral oils with an evaporation loss less than 20 mass%. This procedure demands the addition of Fe_2O_3 as catalyst to 40 mL of oil sample and an air flow of 15 L/h brought in contact with the oil. The test temperature is kept at 200 °C for an alteration duration of 24 h. Afterwards, the

Conradson carbon residue in (mass%) and the evaporation loss as weight change before and after alteration are measured.

Standard **ASTM D 2070** [4.17] determines the thermal stability of hydrocarbon based hydraulic oils in the presence of the catalytic metals copper and iron. A 250 mL glass beaker is filled with a 200 mL aliquot of testing oil, copper, and iron rods and subsequently heated in an aluminium block in an electric gravity convection oven to 135 °C for 168 h. The catalytic rods with a diameter greater than 6.2 mm have to be crossed with contact in only one point and totally emerged in the oil. As preparation, they have to be polished with a 320-grit silicon carbide abrasive cloth and afterwards cleaned to obtain a fresh metal surface.

Upon test completion, the appearance of the metal rods after washing with heptane is evaluated by comparison with the Cincinnati Milacron color chart according to their discoloration. Furthermore, a quantification of the oil sample sludge is done by filtration and gravimetric measurement.

In the standard **ASTM D 5846** [4.18], the oxidation stability of petroleum based hydraulic oils and oils for steam and gas turbines is determined using the universal oxidation test apparatus described in [4.4] (see section 4.2.1.1). For that test, 100 g of oil sample are brought in contact with copper and iron coils as well as with air at a flow rate of 3 L/h in a heating block kept at 135 °C. The coils are made from 0.5 m wires, cleaned with heptane or other saturated paraffinic solvent of comparable boiling point, and afterwards polished with a 100 grit silicon carbide abrasive cloth. All loose particles of metal and abrasives are removed with a dry absorbent cotton. Afterwards, a single coil with an inside diameter of 15.9 to 16.5 mm and a length of 80 mm is formed from the wire.

Sampling of 2 g aliquots is done in one-day intervals determining acid number as well as monitoring sludge formation by spot forming tendency of the tested oil. The latter is evaluated by placing a drop of oil onto a filter paper. The beginning of insoluble formation is indicated by the appearance of a clearly defined dark spot surrounded by a ring of clear oil. Sampling should be carried out even more often when the acid number starts to increase rapidly for a more precise determination.

The end of test is reached when the oil is degraded proved either by an acid number increase of 0.5 mg KOH/g compared to the fresh oil or by on-set of sludge formation. The oxidation life of the oil is reported either as the number of hours until the prescribed increase of 0.5 mg KOH/g in acid number is achieved or as the number of hours until the spot forming tendency indicates sludge development, depending on which incident is first detected.

Standard **DIN EN ISO 4263** describes the so-called turbine oil oxidation stability test (TOST) and consists of four parts designated for different oil types:

Part 1 [4.19] describes a procedure for the determination of the alteration behaviour of mineral oils (especially for turbine oils, categories GL, HM, HR, HV, HG hydraulic fluids, or category CKB circulating oils) with additives (antioxidants, corrosion inhibitors).

300 mL of oil and 60 mL of water are kept at 95 °C without light in a heating oil bath or metal block bath. Oxygen with a constant flow of 3 L/h is bubbled through the oil-water mixture and a double coil of steel and copper is immersed. The coils are made from steel wires with a 1.6 mm diameter and from copper wire with 1.63 mm of diameter. 3 m of each wire are cleaned with heptane, polished with silicon carbide abrasive cloth (100 grit) and afterwards cleaned with dry cloth. The fabrication of the double coil with a total length of 225 mm is performed by means of a hand winch. The oxidation cell is made of borosilicate equipped with a mushroom type condenser with water cooling and an oxygen supply tube (also borosilicate), schematically depicted in Figure 17.

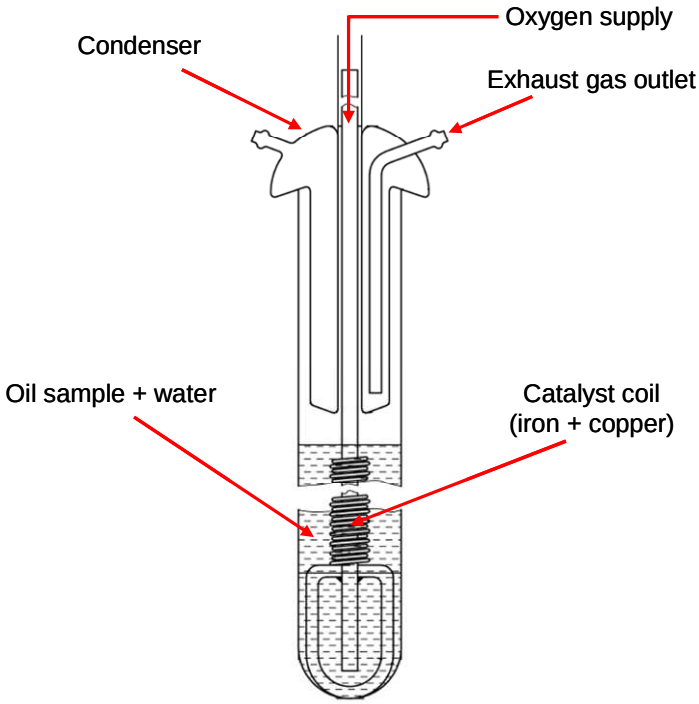

Figure 17: Alteration device for DIN EN ISO 4263 applied in Part 1(modified from [4.19])

Condition monitoring is done by regular sampling of small aliquots in defined intervals of 50 ± 5 h and determination of the acid number thereof. The amount of taken sample has to be restocked by fresh fluid to maintain the liquid level. The end of ageing is reached when an acid number of 2.0 mg KOH/g is observed or after a predefined test duration.

As result, the oxidation lifetime L in hours is calculated by equation

$$L = A + (B - A)\,[(2.0 - C)/(D - C)]$$

with A as time in (hours) from last sample with acid number < 2.0 mg KOH/g, B as time in (hours) from first sample with acid number > 2.0 mg KOH/g, C describing acid number after A hours, and D standing for the acid number after B hours.

Not mandatory but for complementary evaluation, methods to quantify the amount of insolubles by filtration, the qualitative evaluation of the appearance of the catalyst coil, and the determination of the metal content in the oil are proposed.

Part 2 [4.20] of standard DIN EN ISO 4263 is specially designed for category HFC hydraulic fluids. The procedure is similar to the method described in Part 1 where the ageing is accelerated by addition of oxygen and metal catalysts at elevated temperatures in the same alteration device (see Figure 17). Slight differences occur regarding the sample amount. In Part 2, 360 mL of oil instead of a mixture of 300 mL oil and 60 mL of water as described in Part 1 are required.

The analyses during condition monitoring comprise the pH value of the oil sample, the amount of insolubles determined by filtration (membrane filter of 0.4 µm) with subsequent gravimetric assessment, and visual evaluation of catalyst coil.

The end of alteration is reached, when the pH value falls under a threshold of 4.0, the content of insolubles increases to > 4.0 mass% or after a defined duration. But it has to be paid attention that the minimum test duration is 200 h.

As test result, the pH value, the content of insolubles, and the condition of the catalyst coil are noted.

In ***Part 3*** [4.21] of standard DIN EN ISO 4263, an anhydrous procedure for synthetic hydraulic fluids of categories HFDR, HFDU, HEES, and HEPG is described with a sample amount of 360 mL and sampling of 2 to 5 mL of oil at defined intervals. The change in acid number compared to the fresh oil is detected.

Optional analyses are – similar to Part 1 – the content of insolubles, the condition evaluation of the catalyst coil, and the metal content of the oil sample.

The end of the test is reached, when an acid number increase of 2.0 mg KOH/g is observed. In special applications, if an acid number increase of 2.0 mg KOH/g has not been achieved yet, the test can be terminated after a predefined duration (e.g. 500 h or 1000 h). After the completion of the test duration, oil parameters such as acid number or others can be determined.

As result of the test, the oxidation lifetime *L* as duration in (hours) (see Part 1) is reported.

An oil ageing method for industrial gear oils of categories CKC, CKD, CKS, CKT is presented in ***Part 4*** [4.22] of standard DIN EN ISO 4263 with significant differences from the three previous parts. An oxidation cell made from borosilicate closed with a slotted cork stopper and equipped with a borosilicate air supply tube is used, schematically depicted in Figure 18. The air flow is adjusted to 10 L/h. The oil alteration is performed by exclusion of light and without the application of catalyst metals for the duration of 312 h. The temperature is regulated according to the oil type: 95 °C for oils of category CKC, 121 °C for oils of category CKD, and 150 °C for oils of category CKS and CKT.

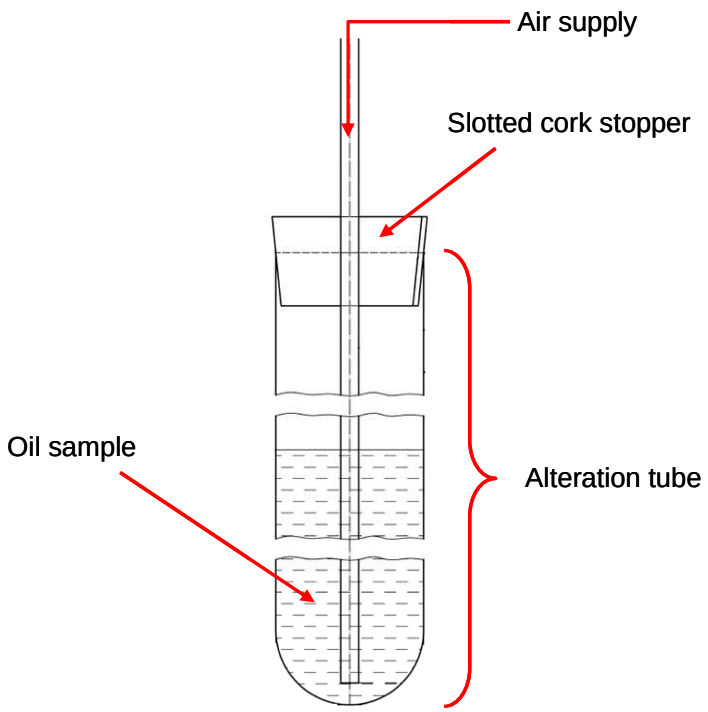

Figure 18: Alteration device for DIN EN ISO 4263 applied in Part 4(modified from [4.22])

After the end of the test, the change in kinematic viscosity at 100 °C, the content of insolubles given as precipitation number, and the appearance of the oxidation cell (presence of deposits) is reported. Optionally, the content of sediments by filtration, the additive degradation by evaluation of the elemental content, and the oxidation by FT-IR can be measured.

4.2.1.4. Thermo-oxidative methods under pressure and with catalysts

A fourth type of oil alteration methods is the connection of all three types presented in the previous sections. Thereby, the oxidative impact of oxygen is combined with the catalytic influence of metals and an alteration accelerating gas pressure.

An example for these methods is described in standard **ASTM D 2272** [4.23] that applies an oxygen pressure vessel to determine the oxidation stability of new and in-service turbine oils in the presence of water and a copper coil. The procedure is used for assessment of the remaining useful life of in-service oils, estimation of oxidation stability and quality control of stability between different oil batches. It is not intended for the comparison of the service lives of differently formulated fresh oils.

For ***method A***, 50 g of oil sample and 5 mL of reagent water added directly to the oil sample are filled in a glass container together with a copper coil. The prepared glass container is then placed in the pressure vessel. Additional 5 mL of water are filled in the vessel outside the glass container. The tightly closed vessel is pressurized with 620 kPa oxygen and kept at the constant temperature of 150 °C in an oil bath. During the test, the vessel is rotated axially at 100 rpm at an angle of 30 ° from the horizontal. A schematic set-up of the rotation device with the inserted pressure vessel is given in Figure 19.

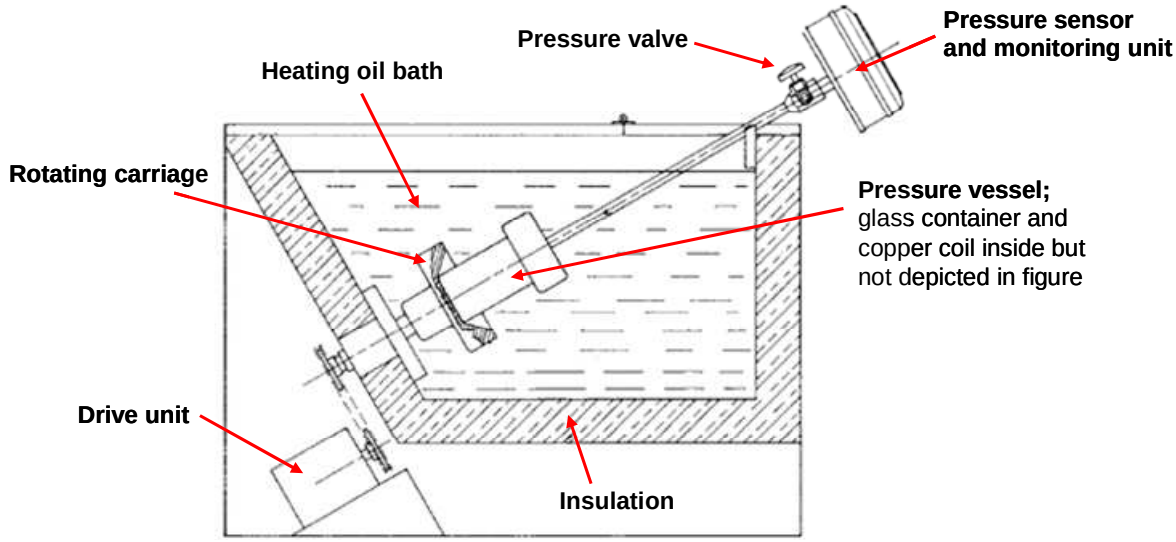

Figure 19: Rotary vessel test apparatus for standard ASTM D 2272 [4.23]

The copper coil is wound from a wire with a diameter of 1.63 mm and a length of 3 m which has to be polished with a silicone carbide abrasive cloth and cleaned with isopropyl alcohol. The dimensions of the coil have to be 44 to 48 mm for the diameter and 40 to 42 mm for the height with a total weight of 55.6 g.

The end of the test is reached, when a defined pressure drop (typically 175 kPa) is reached. The number of minutes until this drop is achieved has to be reported.

Method B is performed with the same parameters as used in method A but the pressure vessel is rotated in a dry metal block bath instrument instead of an oil bath.

A second example for the determination of oxidation stability based on the impact of metals and gas pressure is explained in standard **ASTM D 2112** [4.24], which is specially designated for the evaluation of inhibited mineral insulating oils. The procedure is similar to [4.23] but is performed at lower temperatures.

4.2.2. Standards for engine oils

In section 4.2.1, it is shown, that a diversity of methods and procedures is currently used for the artificial alteration of various oil types and the simulation of different field applications. In this section, the focus is laid on standards describing methods specially designed for engine oils.

Standard **ASTM D 4742** [4.25] investigates the oxidation stability of engine oils for gasoline automotive engines with a viscosity at 100 °C in the range of 4 to 21 mm^2/s in the presence of a metal catalyst package, a fuel catalyst, and water to simulate the conditions a oil has to sustain in a gasoline combustion engine. The method should be used as bench screening test and for quality control, but is not intended to substitute engine bench tests where several other parameters, e.g. wear, volatility, or deposit control characteristics, are measured.

In this manner, 1.500 g of oil are mixed with the following three liquids in a glass container: 0.060 g of an oxidized/nitrated fuel component; 0.060 g of a mixture of soluble metal naphthenates (lead, copper, iron, manganese, and tin); and 0.030 g reagent water. The container with oil mixture is subsequently placed in a high pressure reactor, charged with oxygen to 620 kPa, positioned in an oil bath at 160 °C and rotated axially with 100 rpm at an angle of 30 ° from the horizontal. Thus, the oil forms a thin film in the vessel enabling a large area of contact between oil and oxygen.

The pressure is monitored over the alteration time and continuously recorded. During the test, a constant slight pressure drop occurs due to oxygen uptake of the oil because of oxidation reactions to a little extent. The test is finished when a rapid decrease of pressure is observed, see exemplary curve in Figure 21. The test result is the time until the break down of the pressure curve which is called the oxidation induction time. This break point is calculated as the intersection of the tangent of the stable pressure curve in the final 20 min before and the tangent of the decreasing pressure trace after the break point, see also Figure 21.

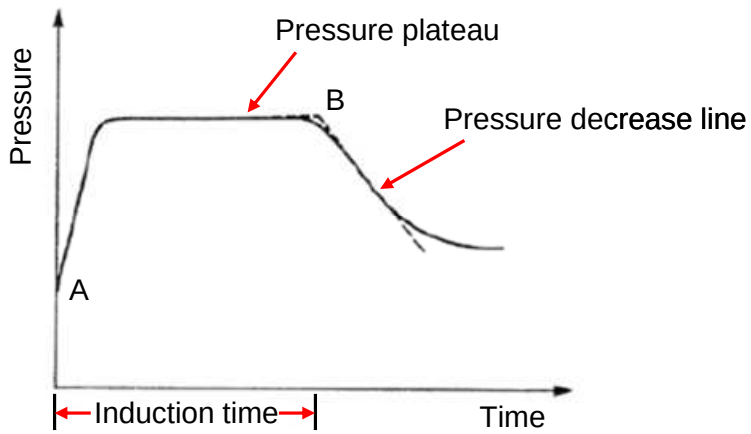

Figure 20: Determination of the induction time [4.25]

Standard **ASTM D 7098** [4.26] is designated to determine the oxidation stability of lubricants by thin-film oxygen uptake (TFOUT) with Catalyst B, originally a screening test for evaluation whether a lubricating oil is applicable as automotive engine oil.

For this test, 1.500 g of the oil are blended with a Catalyst B package of four components: 0.030 g of a oxidized/nitrated fuel component; 0.045 g of a mixture of soluble metal naphthenates (lead, iron, manganese, and tin); 0.030 g of a nitro-paraffinic compound; and 0.030 g reagent water. The testing parameters, the accomplishment, and the reporting are analogous to [4.25].

A different approach to the investigation of engine oils is standard **ASTM D 6335** [4.27], which determines the quantity of deposits formed by means of the thermo-oxidation engine oil simulation test (TEOST). By this method, a prediction of the high temperature deposit formation tendency of engine oils is enabled.

A schematic drawing of the device is shown in Figure 21.

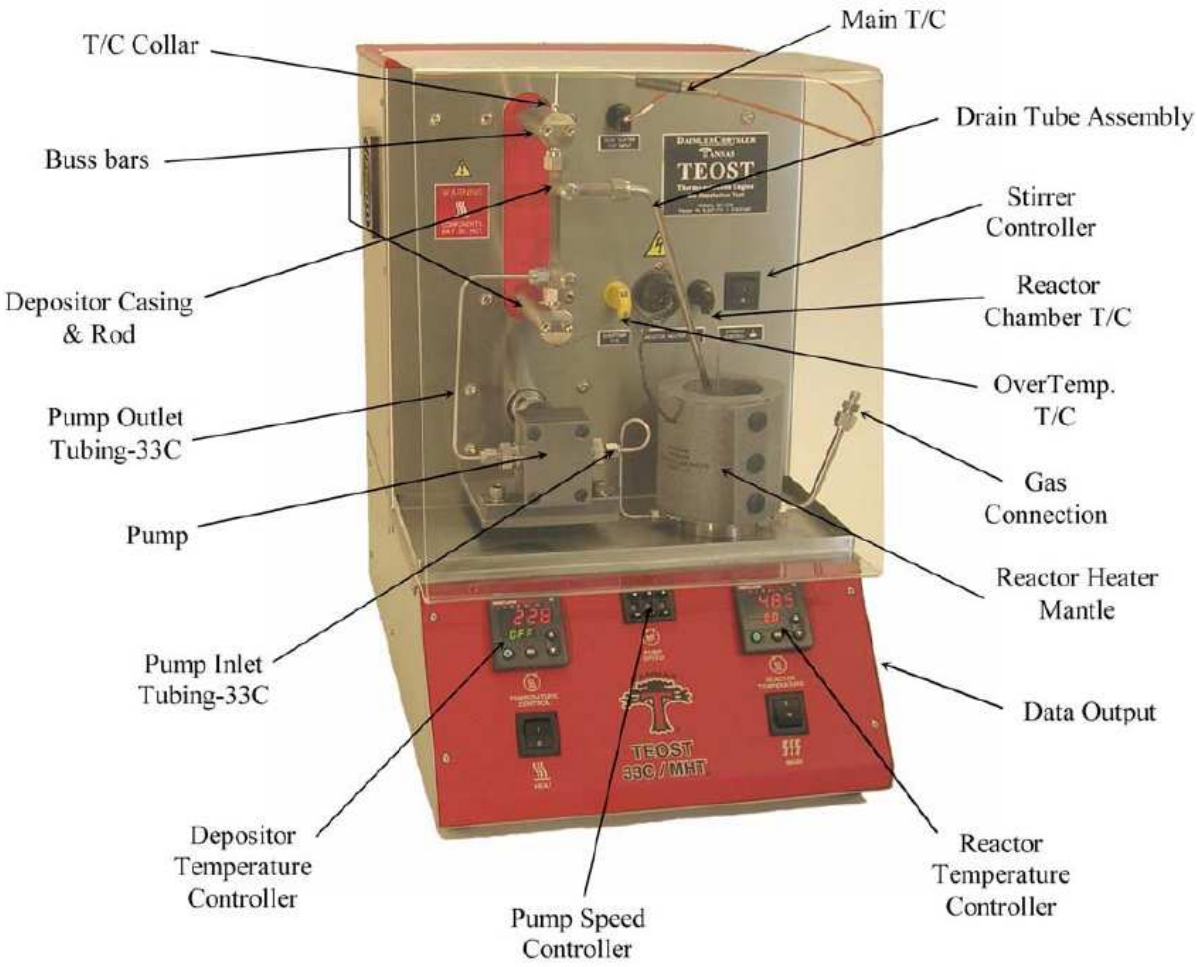

Figure 21: Schematic drawing of the thermo-oxidation engine oil simulation test (TEOST) [4.27]

116 mL of testing oil are blended with 193 µL of 6 % iron (II) salt of naphtenic acid solution in a 600 mL beaker with a resulting iron concentration in the test fluid of ~ 100 wt ppm. This blend is inserted into the TEOST device, where the sample is brought in contact with nitrous oxides and moist air at 100 °C. Subsequently, it is pumped past a tared depositor rod with a flow rate of 0.49 mL/min, which is heated resistively according to a defined temperature program – twelve circles of each 9.5 min with temperatures ranging from 200 to 480 °C and a test time of 1 h 45 min. After the performance of twelve circles, the depositor rod is cleaned so that it appears oil free, dried, and weighted. The oil sample is collected and filtered.

As test result, the sum of the deposit mass measured in the rod and on the filter is reported.

An evaluation of the amount of deposits formed on a wire-wound depositor rod is presented in **ASTM D 7097** [4.28], where the performance of the moderately high temperature thermo-oxidation engine oil simulation test (TEOST MHT) is described. By the test, a prediction of

the deposit formation tendency in the piston ring belt and the upper piston crown area is facilitated.

The patented instrument to carry out this test is shown in Figure 22.

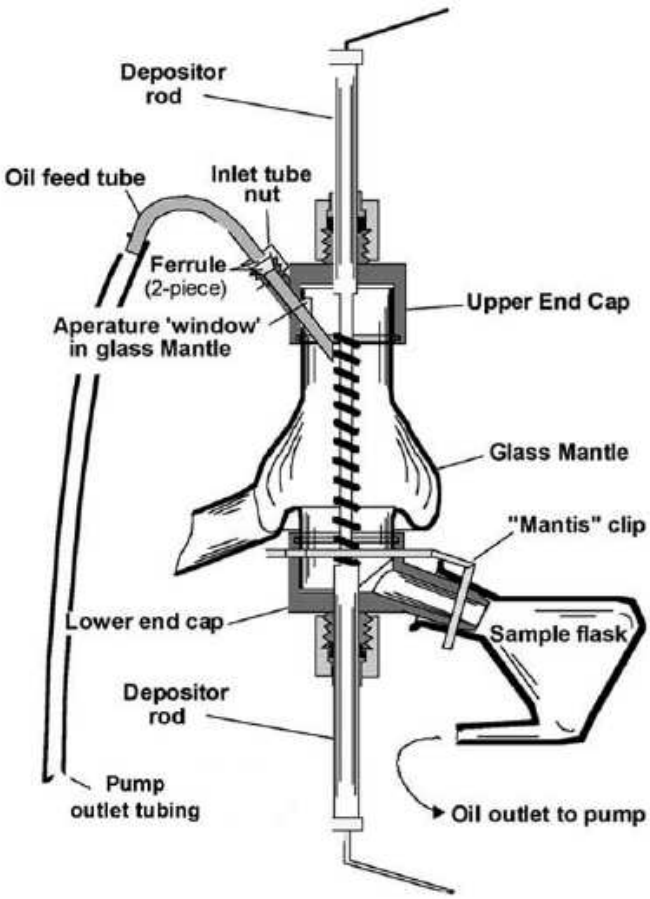

Figure 22: Schematic drawing of the TEOST MHT [4.28]

The testing oil is blended with an organo-metallic catalyst containing iron, lead, and tin in suitable ratios for the simulation of engine deposit conditions with a total weight of 8.5 g. This blend is repetitively passed over the depositor rod in a thin film under oxidative and catalytic conditions. The rod is heated electrically to 285 °C, oil flow rate is 0.25 g/min and one circle has the duration of 24 h. During test, a controlled and directed dry air flow of 10 mL/min is in contact with the oil on the depositor rod giving the opportunity for oxidation processes.

The result of the test comprises the weight of deposits formed on the rod determined gravimetrically as mass difference before and after the experiment, the mass of deposits in the oil mixture measured by filtration as well as the total mass of deposits formed during the experiment.

4.2.3. Critical consideration of currently applied standards especially concerning bio-fuels

As shown in the previous sub-chapters, artificial alteration means applying harsh conditions to an oil aliquot to accelerate oil degradation at a very short-term scale. Most standards examine the thermal-oxidative stability of lubricating oils by exposing them to elevated temperatures and oxygen. Partly, they use metallic catalysts; other procedures investigate the potential for deposit development of oils at high temperatures or their corrosiveness on different reference metals. In some cases, artificial alteration is carried out under pressure in specially designed vessels.

Despite of this, the most important demand on an artificial alteration procedure is the consideration of the relevant oil degradation mechanisms occurring under the respective real operating conditions, which should be simulated in the laboratory.

Concerning bio-fuel alteration evaluation, no standard being currently in use evaluates the impact of unburnt or partially combusted fuel components that can be taken up by the engine oil via blow-by gases. Hence, the afore mentioned artificial alteration methods are not able to provide satisfactory knowledge about the lubricant performance under the special conditions emerging from fuels containing compounds originating from renewable resources, especially on a long-term base. Arising from current developments in fuel composition with increasing content of bio-components, novel artificial alteration procedures with stronger consideration of this special application have to be introduced. Various benefits compared to existing standard methods could be expected, e.g. a deeper insight in complex alteration mechanisms depending on the engine oil quality, the possibility of a long-term study of the oil performance even far beyond conventional oil drain intervals, and the provision of an economic as well as efficient tool for the pre-selection of future oil formulations resulting in a lower number of candidate formulations for expensive and time-consuming engine bench tests. [4.29]

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5. Chemometrics as data processing tool

Chemometrics is defined as "*a chemical discipline that uses statistical and mathematical methods, to design or select optimum procedures and experiments, and to provide maximum chemical information by analyzing chemical data*" [5.1]. Or in other words, an "*extraction of relevant information from chemical data by mathematical and statistical tools*" should be achieved by this means. Chemometrics can be regarded as being a discipline combining measured-orientated chemistry with applied statistics [5.1].

Typical questions, the chemometric approach is dealing with, are [5.1]

- concentration determination of a single compound in a complex mixture (often done e.g. by data derived from infrared spectra),
- origin classification of different samples (mainly from chemical analytical or spectroscopic data),
- property or activity prediction of unknown chemical compounds on the base of identified substances with similar chemistry (with data derived from chemical structure data),
- presence and/or absence recognition of chemical substructures in unknown molecules (with spectroscopic data evaluation), and
- process status evaluation in chemical technology (with data measured by spectroscopic and other analytical means).

In spite of the broad definition of chemometrics, its most important area is the multivariate data analysis of chemically derived data where relationships between a large number of samples described by multiple measurements have to be found [5.1].

Multivariate data analysis comprises three main fields [5.2, 5.3]:

1. Exploratory data analysis, cluster analysis

   This approach is used to determine outliers in a set of multivariate data as well as to discover patterns and trends.

   The method utilized is the principal component analysis (PCA, see below), an exploratory algorithm, which enables the most representative imaging of multivariate data in a compact data table. In doing so, the minimisation of a large quantity of data that characterise samples into a manageable amount is achieved to reveal similarities and differences between these samples, which would not be possible by conventional analytical tools due to the large amount of variables.

2. Multivariate calibration, regression

   The fundamental aim in science and technology is the modelling of a property *y* by one or several variables *x*, whereupon it is not possible to determine *y* directly or only in connection with high costs whereas *x*-data are easily available. Sometimes the relationship between *x* and *y* can be described by a fundamental scientific law, sometimes it can be defined by a relatively simple mathematical equation. But in many cases, no obvious mathematical relationships exist to determine the correlation of *x* and *y*.

   Examples cover modelling of the boiling point or the toxicity of chemical compounds by chemical structure variables. These investigations, quantitative structure-property or structure-activity relationships (QSPR/QSAR) require the application of multivariate calibration models. Thereby, a model is developed to find the correlation between *x* and the unknown but desired property *y*.

   For multivariate calibration, the commonly utilized chemometric algorithms are the partial least square regression (PLS), see [5.4] and [5.5] as well as the principal component regression (PCR), see [5.5].

   This chemometric approach is extensively applied by on-line monitoring quality management and in process control.

3. Multivariate classification

   This method is applied for the prediction of the assignment of a respective sample to a certain group of predefined categories based on examples of properties which are as close as possible to the unknown object.

   Typical applications of this method are the classification of the origin of a sample, the taxonomy of bacteria or plants, detection of diseases from clinical-chemical data, the identification of chemical substructures from spectroscopy, or the classification of chemical compounds regarding their activity, property, or reactivity.

   Accordingly, strategies frequently used for classification are

   - utilisation of linear latent variables, e.g. the linear discriminant analysis (LDA), see [5.6] and [5.7],
   - modelling of object classes by prototypes, hyper-boxes (soft independent modelling of class analogy, SIMCA), see [5.7], or hyperellipsoids (Mahalanobis distance), see [5.8],
   - k-nearest neighbour (kNN) classification, see [5.9],
   - classification trees, see [5.10],

- support vector machines (SVM), see [5.4, 5.6, 5.7, 5.9],
- artificial neural networks (ANN), see [5.4, 5.9], and
- visualisation of objects (Chernoff faces), see [5.11].

PCA, "*the mother of all methods in multivariate data analysis*" [5.1], is a simple, non-parametric method for the extraction of relevant information from highly complex data sets, thus reducing them to a lower number of dimensions offering insight in sometimes covered interrelations [5.12].

It uses so called latent ("hidden") variables to optimally represent the multidimensional structure of a data set. Latent variables (also called components or factors) are formal linear combinations of the original variables (also called **features**), which depict the Euclidean distance as an inverse measure of similarity between the respective samples (also called **objects**). They are calculated from all m features of a sample, hence summarising them and representing a projection of the points in the m-dimensional feature space onto a straight line [5.2, 5.13, 5.14].

Each latent variable is described by a linear combination according to following equation:

$$u = b_1x_1 + b_2x_2 + \ldots + b_mx_m \qquad [5.2]$$

whereupon u is the value of the latent variable, also called **score**; b denotes the coefficient describing the contribution of a feature to the score, also called **loading**; and x stands for the feature.

All variables form an object vector $\boldsymbol{x} = (x_1, \ldots, x_m)^T$ [5.2], the loadings form a respective loading vector $\boldsymbol{b} = (b_1, \ldots, b_m)^T$ [5.2], usually scaled to the length of 1. Derivatively, the score can be determined as the scalar product thereof such as $u = \boldsymbol{x}^T * \boldsymbol{b}$ [5.2].

Figure 23 illustrates the application of multivariate data analysis on the example of infrared spectra of various oil samples after artificial alteration and alteration in an engine for the mathematical determination of the Total Acid Number.

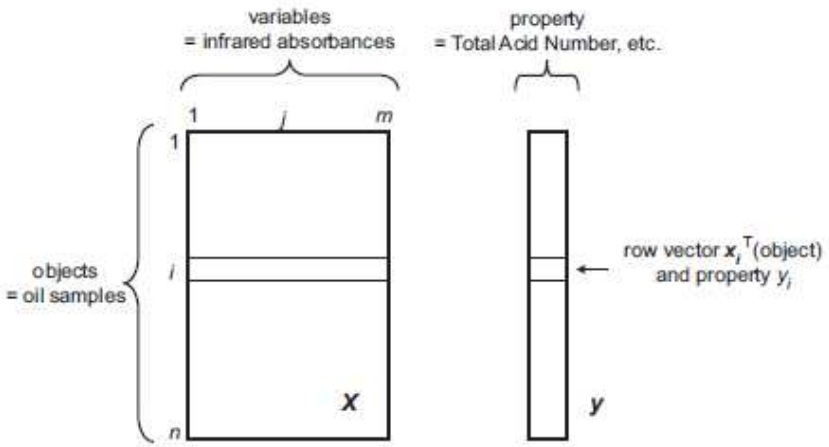

Figure 23: Schematic illustration of multivariate data analysis [5.14]

Depending on the desired aim of the data analysis, latent variables are defined by different mathematical criteria. In the case of PCA, the criterion is the maximum variance of the scores resulting in an optimum illustration of the Euclidean distance between the respective objects as an inverse measure of similarity. The direction with the maximum variance is called the first principal component (PC1). The second principal component (PC2) is orthogonal to PC1 and again depicts the direction of the maximum possible and residual variance (see Figure 24). Further principal components up to the number of features can be determined according to the same procedure. Calculation of all PCs represents a rotation of the *m*-dimensional feature space [5.1, 5.2].

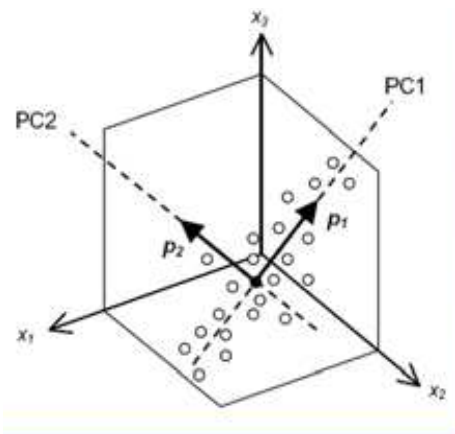

Figure 24: Principal components PC1 and PC2
as axes of a new Cartesian coordinate system [5.2]

Scores and loadings can be illustrated in scatter plots – score plots and loading plots, respectively – offering the possibility to plot various PCs against each other, e.g. PC1 versus PC2, PC1 versus PC3, PC2 versus PC3.

Exemplarily, Figure 25 and Figure 26 show the score plot and the loading plot, respectively, of the PCA of various oil samples as described in Figure 23. Each data point stands for one sample in the score plot or for one variable, i.e. one IR absorbance wave number, in the loadings plot.

By the evaluation of the score plot, different alteration conditions – here artificial and engine alteration – can be clearly differentiated. Even the impact of acetic acid can be visualised. Information about the reasons for these differences can be found in the respective loading plot. Obviously, the absorbances between wave numbers of 1615-1650 cm^{-1} (specific for nitration products) and 960-990 cm^{-1} (specific for antiwear additives) are in the area of engine alteration, whereas absorbances at wave numbers of 3645-3655 cm^{-1} (specific for phenolic antioxidants) appear in the area of artificial alteration and absorbances at wave numbers between 1708-1760 cm^{-1} (specific for oxidation products) can be contributed to both alteration conditions. These findings imply that antiwear additives are less degraded in the engine alteration but phenolic antioxidants are more stable under the conditions of artificial alteration. Furthermore, nitration processes are far more pronounced under engine application whereas oxidation processes occur in artificial as well as in engine alteration.

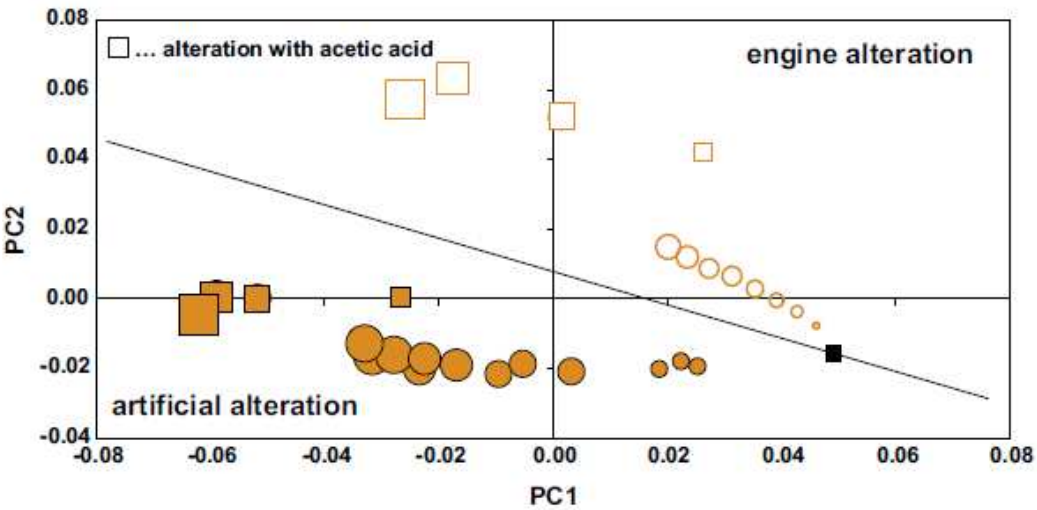

Figure 25: PCA score plot of oil samples from artificial alteration and engine alteration with and without addition of acetic acid

Note: Full diagonal line emphasises the border between artificial alteration and alteration in the engine; circles depict reference alterations, alterations with ethanol and alterations with acetaldehyde, squares depict alterations with acetic acid; full symbols indicate alteration in the laboratory, empty symbols indicate alteration in the engine [5.14]

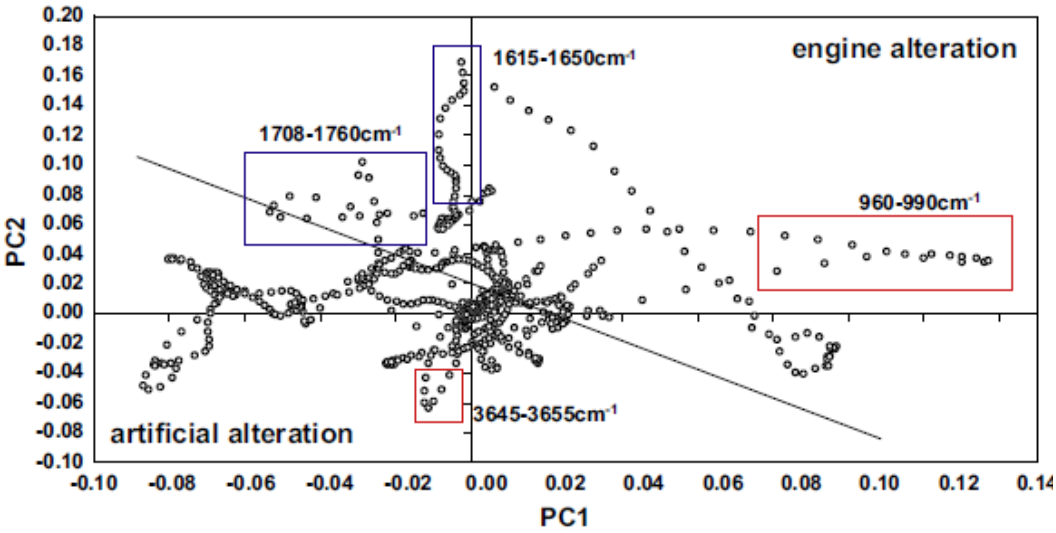

Figure 26: PCA loading plot of oil samples from artificial alteration and engine alteration with and without addition of acetic acid

Note: Variables in the red boxes stand for additives, ZDDP (960 – 990cm^{-1}) and phenolic antioxidants (3645 – 3655cm^{-1}), respectively;

variables in the blue boxes stand for oil degradation products, oxidation (1708 – 1760cm^{-1}) and nitration (1615 – 1650 cm^{-1}), respectively [5.14]

The above-mentioned example demonstrates the valuable input of PCA application when dealing with large amounts of data such as infrared data in the field of oil condition monitoring.

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PART B: Experimental, results, and conclusions

1. Objective target of the thesis

Due to the fact that the knowledge about the impact of bio-ethanol and its partial combustion products on the engine oil performance is fairly limited, the first aim of the thesis is the set-up of a **novel artificial oil alteration method** for a closer-to reality simulation of conditions predominating in an engine fuelled with bio-ethanol blended gasoline. In doing so, the engine oil condition should be evaluated by monitoring conventional oil alteration parameters as well as by applying advanced analytical methods. Special attention should be paid to the physical appearance of the oil samples, i.e. turbidity or sludge formation, connected with an in-depth morphological analysis of potential precipitation, e.g. by scanning electron microscopy. The potential of the novel artificial alteration method should be verified by offering valuable input for the consecutive improvement of oil formulations.

Results achieved during artificial alteration in the laboratory should be expanded by experiments made under near-real conditions. In doing so, oils already evaluated in the lab should be applied in **chassis dynamometer bench tests**. By continuous oil condition monitoring, a deeper insight in oil degradation processes should be gained. Furthermore, failure assessment should be carried out on engine parts demounted from the operated passenger car to characterise the engine condition concerning corrosion and wear. Findings obtained should be compared to data from static corrosion experiments carried out in the laboratory.

The third objective of the thesis comprises the evaluation and comparison of all oil condition data collected, i.e. from the laboratory as well as from the dynamometer bench test. In this manner, the method of choice should be the chemometric approach of **Principal Component Analysis (PCA)**, whereby similarities and differences respectively should be revealed of oil samples from both alteration conditions evaluating the correlation between artificial alteration in the laboratory and in the engine system. At the same time, the usefulness of statistical mathematical techniques for the investigation of engine oil degradation should be evaluated.

2. Publications within the thesis topic

2.1. Investigation of long-term engine oil performance using lab-based artificial ageing illustrated by the impact of ethanol as fuel component

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Investigation of long-term engine oil performance using lab-based artificial ageing illustrated by the impact of ethanol as fuel component

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ABSTRACT

The effect of ethanol and its combustion products on the lubrication system is not very well understood. In this paper, a novel lab-based artificial ageing method for the evaluation of engine oils for bio-fuelled automotives and the results thereof are presented. Artificial ageing of three fully formulated engine oils with addition of ethanol, acetaldehyde, and acetic acid was carried out. The oil formulations chosen represent a consequent series of optimisation steps based on the engine oil performance in terms of preservation of typical oil parameters, e.g. base reserve and oxidation, observed during the artificial ageing procedure. It was shown that ethanol as well as acetaldehyde has almost no effect on the oil degradation especially in the case that advanced additive technology was used. On the contrary, acetic acid significantly affected the formulated oil showing influence on the detergent chemistry and even caused sludge formation. The use of the novel artificial ageing method proved to clearly differentiate the impact of the respective compounds added with the possibility to simulate enhanced stress conditions without the need of time-consuming and expensive engine bench tests. Hence, the novel setup offers valuable input for the formulation and the pre-selection of future engine oils suitable for bio-fuel.

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1. Introduction

1.1. General introduction

In recent years, there has been a growing interest in the use of bio-fuels. The main reasons for this worldwide interest are the awareness of the limitation of fossil fuel resources closely linked with the increase of oil prices, the reliability of supply, and hence the interest in the reduction of the dependence on foreign petroleum resources. Additionally, global warming gains increase the significance and so the need for a drastic reduction of CO_2 emissions.

These strategic, economical and environmental issues found their way into legislation related to energy and fuel, respectively, and had a direct impact on the formulation of fuels. In May 2003, the European Union released the directive 2003/30/EC [1], commonly known as the 'bio-fuels directive'. This non-binding directive asked for replacing 2% of all transport-related fossil fuels by bio-fuels until December 31, 2005, and required a further increase in substitution to 5.75% until December 31, 2010. In 2009, the directive 2003/30/EC was replaced by the now binding directive 2009/28/EC [2] with the mandatory target to replace 10% of common fuels by bio-components until 2020.

When using bio-fuels as an additional component in fuels for automobiles, bio-diesel for diesel and ethanol for gasoline engines are very commonly utilised. Bio-diesel and its impact on the engine performance, emission profile and the lubrication system have been the object of intense research: Sinha et al. analysed deposit formation and carried out long-term endurance tests [3]. Borrás et al. investigated the exhaust emissions of light-duty diesel engines and found rape oil methyl ester bio-diesel to be effective in reducing polycyclic hydrocarbon (PAH) emission [4]. Jain et al. presented an overview over the different aspects of stability of bio-diesel. Methods to measure and improve the stability were mentioned in this publication [5]. There are various papers that report about fuel dilution of engine oil by bio-diesel and the resulting effects. Peacock et al. found for example an accumulation of 0.5% fatty acid methyl ester (FAME) in the lubrication system after 3240 km car operation [6]. Non-published experience indicates that an uptake between 5% and 10% of bio-diesel into lubricants is very common. At the end of oil change intervals elevated contents up to 20% of bio-diesel in the oil are possible and were found.

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On the other hand, alcohols such as methanol and ethanol have to be considered as a serious alternative to fossil gasoline. The global production of fuel ethanol increased from 31.3 billion litres in 2005 to over 85.6 billion litres in 2010 [7]. Ethanol for example offers a variety of benefits, due to different aspects [8]: it is available from renewable resources and therefore CO_2 neutral; ethanol possesses positive properties for the use in internal combustion engines, e.g. higher auto ignition endurance due to a research octane number between 100 and 106, enabling this way higher compression ratios and engine efficiency as well as the increase in specific power; its broader inflammable limit allows adjustments of leaner fuel mixtures with about 15%; besides, it is stable in common tanks at room temperature and does not undergo accidental polymerisation as observed for some other fuel components with low stability; for storage and transportation, the existing infrastructure for fossil fuel distribution can be used; finally, the dependence of foreign fossil fuel import is decreased and a source of higher revenue for the local agriculture system is created, which is heavily discussed due to replacement of farmland.

Countries offering commercially available fuels with high amounts of ethanol also show increased use of flexi fuel vehicles (FFV). USA, Sweden and in particular Brazil with ethanol contents of 25 vol% [9] and more have to be mentioned in this context. There significantly shortened oil change intervals are observed. But a direct comparison between the oil drain intervals in European and Brazilian vehicles cannot be drawn due to different levels of engine and oil technology, respectively, and the different climates.

In former years, the influence of methanol on the engine was the object of quite a number of investigations. For example, Moritani et al. showed that blends of methanol and gasoline caused less sludge formation, in particular at methanol concentrations higher than 50 vol% [10]. Shah et al. carried out oxidation stability and wear tests with different lubricants designed for the application in methanol fuelled cars. They showed that contamination with methanol could separate additives and less viscous portions of the base oil by some kind of liquid–liquid extraction, which led to reduced oxidation stability and declined wear properties [11].

In contrast to this, the effect of ethanol on the lubrication system is still not well known and therefore a strong need for detailed investigations is given. Because of its high volatility (boiling point of 78 °C at 1 bar) it usually easily evaporates out of the lubrication system. Nevertheless, partial combustion can form more reactive compounds emerging from ethanol, which could be accumulated in the engine oil. There are reports, which show the presence of increased levels of ethanol and water in the lubrication system after certain driving conditions. Boons et al., for example, carried out a field test with 85% ethanol–gasoline-blends in cold climate and with short driving cycles. They found significantly higher contents of water and ethanol in the lubricant, but no problems in the engine or driving performance have been observed [12].

Additionally, complementary investigations examined the impact of ethanol on the emission characteristics of different engines. Maheshwari et al. found out that ethanol reduces emissions of carbon monoxide (CO) from two-wheelers but slightly increases of hydrocarbon (HC) emission. However, in passenger cars both the CO and the HC emissions are significantly decreased, but on the other hand the content of nitrogen oxides marginally increased [13]. Tseng et al. stated a significantly increase of 41.3% in the exhaust of acetaldehyde by motorcycles when using 3% ethanol in gasoline [14]. Ginnebaugh et al. showed in their studies that the level of formaldehyde, acetaldehyde, and peroxyacyl nitrates (PAN) in the emissions of vehicles was much higher during the use of a blend of gasoline with 85% of ethanol than with neat gasoline [15]. Gaffney et al. stated that ethanol combustion causes development of acetaldehyde, which in turn is responsible for the formation of products like ozone, H_2O_2, formic acid, and CO, as well as PANs and peracetic acid [16]. Chen et al. found out that the optimum ethanol content in gasoline for cold starting conditions lies between 20% and 30% concerning emission characteristics [17].

Given the matter of facts above, there is an obvious demand to accomplish in-depth investigation to reveal the impact of components from renewable resources in fuels on the lubrication system.

1.2. Fuel specific consideration of artificial ageing of engine oils

Artificial ageing means applying harsh conditions to the oil sample to accelerate oil degradation at a very short-term scale. Nevertheless an artificial ageing procedure should consider the relevant oil degradation mechanisms occurring under real engine operating conditions.

Currently used standardized methods for the artificial ageing of lubricating oils evaluate different parameters of the oil performance. Most standards examine the thermal-oxidative stability of oils by exposing it to elevated temperatures and oxygen from air [18,19]. Partly, they use metallic catalysts to accelerate ageing or lubricant degradation [20,21]. Other procedures investigate the potential for deposit development of oils at high temperatures [22,23] or the corrosiveness of oils on different reference metals is tested [24].

But no standard being currently in use evaluates the impact of unburnt or partially combusted fuel components that are taken up by the engine oil via blow-by gases. In particular, the impact of bio-fuel on the oil is not considered. Hence, the aforementioned artificial ageing procedures cannot provide satisfactory knowledge about the lubricant performance under the special conditions emerging from fuels containing bio-components, especially on a long-term basis.

Dealing with the new circumstances in bio-fuelled engines, new artificial ageing methods with strong connection to this special application have to be introduced. Requirements of these procedures are the consideration of fuel components as well as combustion products thereof, the contemplation of different oil types like automotive or stationary engine oil, the investigation of oil degradation caused by these compounds by regular sampling and oil condition monitoring, the economic simulation of engine procedures.

The following valuable benefits in comparison to existing test methods are expected by the implementation of a novel artificial ageing method: a knowledge gain in complex ageing mechanisms according to engine oil quality, the study of the long-term performance even far beyond conventional oil drain intervals being relevant for the knowledge of oil failure, and economic as well as efficient means of evaluating novel oil formulations by pre-selection and hence reduction of candidate formulations for time-consuming and expensive engine bench tests.

Based on these requirements and targets a novel lab-based artificial ageing method was developed. This paper presents the first use of the method and first results in an intense study carried out as a fundamental research on lubricant deterioration and investigation of deterioration mechanisms. The focus is to evaluate the potential of the method illustrated by the development of new engine oil formulations. These oils have been optimised for the use of ethanol containing fuels.

It will be demonstrated that the limitations exhibited by standardized methods have been overcome by the addition of typical compounds caused by bio-fuel to the oil during artificial

ageing. Fuel induced lubricant degradation has been induced and accompanied by oil condition monitoring. Usually, oil analysis is performed after a certain ageing time defined by the standards and limited to a small number of oil parameters such as acid number. For this reason, oil analysis has been performed by regular sampling too and as an indispensable tool to understand the occurring ageing mechanisms.

2. Experimental

2.1. General artificial ageing procedure—reference ageing with air

Fig. 1 shows that the novel artificial ageing device enabled the adjustment of specifically defined conditions. Thereby, the lubricant oil is placed in a round bottomed three-neck glass flask equipped with a cooling device at neck 1 and kept at a defined temperature by a heating oil bath. The oil is brought into contact with dried air via glass tube through neck 2. The air gas flow is adjusted by a flow controller. Neck 3 of the flask is intended for periodical sampling and condition monitoring. Oil vapours contaminating the exhaust gases can be removed by washing flasks and be collected for further analysis. The oil temperature as well as the air flow can be adapted to the particular conditions. The oil sample is not exposed to light to avoid the influence of ultraviolet radiation, i.e. induction of photochemical reactions.

This artificial ageing with air was carried out on the basis of [19] and should serve as a reference for comparison of the selected engine oils' performance applying a currently used standard with the results achieved with the novel artificial ageing method.

The artificial ageing procedures were commonly carried out at certain technical characteristics. Due to the fact that the main deterioration of the lubricant takes place in the combustion chamber, the temperature of the oil sample was constantly held at 160 °C to simulate conditions prevailing in the area of the piston rings [25]. The dried air flow was adjusted at 10 L/h, and the test duration was always 96 h. The amount of oil sample introduced in the flask was 300 g.

2.2. Definition of parameters for oil condition monitoring

The influence of fuel induced lubricant degradation on the lubricant properties has been deduced from several oil parameters analysed from the oil samples obtained. Visual evaluation was also done. The determination of the oxidation value was carried out by Fourier Transformation infrared spectroscopy using standard DIN 51453 [26]. Therein the oxidation given in absorbance per cm is calculated at the wavelength of 1710 cm^{-1} utilising the formula: oxidation (A/cm)=extinction (A)/thickness of cuvette (cm). The Total Base Number (TBN) is determined using standard DIN ISO 3771 [27] by potentiometric perchloric titration and depicts the amount of perchloric acid in equivalent mg of potassium hydroxide, which is required to neutralise all basic components in 1 g of oil sample. As additional parameter the Neutralization Number (NN) was measured using standard DIN 51558 [28], which defines NN as the amount of base needed to neutralise all acid components in 1 g of oil sample. For all artificial ageing procedures applied sampling of aliquot amounts of about 15 mL was done every 24 h.

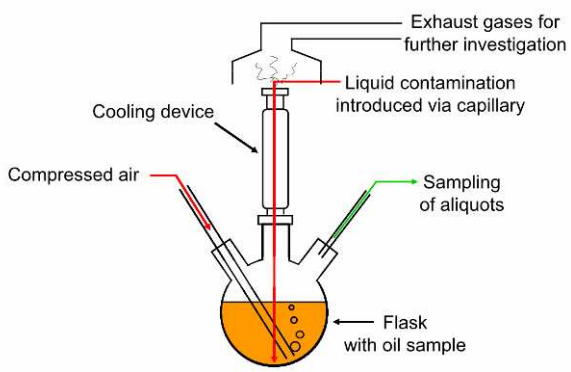

Fig. 1. Schematic setup of the novel ageing method, the simulation of fuel induced oil deterioration is realised by the addition of liquid via a Teflon tube in the cooler.

2.3. Ageing with addition of bio-ethanol related compounds

Ageing with additional compounds (see below) was carried out as described above, but the device was equipped additionally with a Teflon tube for the introduction of liquids. This way, the lubrication oil can be exposed to the special conditions caused by components derived from fuels during the ageing process as depicted in Fig. 1. In detail, the influence of bio-components in fuel and afterwards in combustion products thereof brought in the lubrication system via blow-by gases and by down-washing from the cylinder liner wall could be simulated.

Three liquid compounds were selected and added to the oil during the whole ageing duration. These liquids were ethanol (absolute for analysis, ≥99.9%, Merck, Darmstadt, Germany), acetaldehyde (for synthesis, ≥99%, Merck, Darmstadt, Germany) as an oxidation product and combustion by-product of ethanol, and acetic acid (for synthesis, ≥99%, Merck, Darmstadt, Germany) as another possible combustion by-product of ethanol from partial oxidation.

The addition of ethanol and acetic acid was achieved with a dosing device via a Teflon tube through the cooler to the bottom of the flask. The sequence of dosing was carried out in small portions during the whole artificial ageing duration. Ethanol was added in two concentrations: on one hand the ethanol amount of 1% of engine oil volume per day was introduced and on the other hand a very high level of 1% of ethanol in relation to the engine oil volume per hour was set up. Acetic acid was added in a concentration of 0.1% of engine oil volume per hour.

Acetaldehyde possesses a high volatility due to the low boiling point of 20 °C. For this reason the dosing device had to be cooled down to ensure that the intended amount of bio-ethanol related compound is added to the oil. To minimise the risk of an explosion in the flask because of a self-ignition of acetaldehyde a special sequence for dosing was developed. The concentration of acetaldehyde was chosen equally to that of acetic acid being 0.1% related to engine oil volume per hour. The quantities of compounds added depict elevated concentrations of amounts experienced to be possible in real engines and were chosen to accelerate artificial ageing.

2.4. Particle analysis

Additionally to the common oil parameters, particles—if formed—originating from the lubricant oil were studied after 96 h of artificial ageing to investigate the morphologies and elemental compositions of the sludge or deposit developed upon oil degradation. For this purpose the scanning electron micrometre Philips XL30 ESEM-FEG coupled with energy dispersive X-Ray analysis (SEM-EDX) (Philips Electron Optics, Amsterdam, The Netherlands) was applied. Images were obtained by a secondary electron detector (SE) displaying the surface properties at high lateral resolution. Additionally a backscattered electron

detector (BSE) was used to produce images with elemental contrast. Besides, elemental composition was determined using EDX (Genesis system with SUTW Window, EDAX)

Particles from selected artificial ageing procedures were separated from the respective samples by suction of the n-heptane diluted oils through a 0.8 μm nitrocellulose filter, then washed three times with approximately 20 mL n-heptane. The deposits were stamped off the filter with an adhesive graphite tape on a sample holder and positioned in the SEM device. SEM images were obtained in secondary electron and backscattered electron mode in high vacuum of minimum 10^{-6} mbar with an acceleration voltage of 20.0 kV. Elemental quantification using EDX was performed at the same conditions with a collection time of 60 s.

2.5. Artificial ageing matrix

For the evaluation of the potential of artificial ageing as proposed above a fully formulated engine oil A with the viscosity grade SAE 15W-40 and containing group I mineral base oil was chosen to represent a common engine oil technology currently available in the market. The performance of this oil during artificial ageing led to the improved formulation of oil B with the viscosity grade SAE 5W-40 and subsequently oil C with the viscosity grade SAE 5W-30. Oils B and C both consisting of group III hydrocrack base oil, and possessing advanced quality in comparison with oil A differ mainly from oil A in terms of different base oils as well as additives. The performance of oil B and oil C regarding the preservation of typical oil parameters was also investigated by means of the novel artificial ageing device.

Considering oil chemistry, the use of hydrocrack base oil instead of mineral base oil resulted in improved viscosity–temperature behaviour expressed as increased viscosity index. Furthermore, oils B and C were formulated with viscosity index improvers resulting in further enhancement of the viscosity–temperature behaviour.

Besides base oil quality, variation in additives—in particular detergents and anti-wear additives—of oils B and C in comparison with oil A is obvious. The presence of high amounts of the element calcium indicates a base reserve and the amount of detergents has been increased significantly in oils B and C. An increase can also be stated for the elements phosphorus and zinc in oils B and C. Furthermore, sulphur, which can be found in both, base oil as well as additives, was present at a reduced concentration mainly attributed to improved base oil quality. Oils A and B were formulated with aminic antioxidants whereas oil C was composed of both aminic and phenolic antioxidants. TBN and NN are sum oil parameters with contribution from all additives with basic or acidic properties. Hence, a comparison of these values in fresh condition with those in aged condition is considered more beneficial than the interpretation of the fresh oil values. Table 1 shows an overview of the main properties of all three oils in fresh condition.

Table 1
Physical–chemical properties of engine oils A, B and C.

Oil parameter	Oil A	Oil B	Oil C
Viscosity 40 °C (mm^2/s)	101	82.4	70.5
Viscosity 100 °C (mm^2/s)	13.7	13.9	11.8
Viscosity index	135	175	164
Density 15 °C (g/cm^3)	0.88	0.85	0.85
Total base number (mg KOH/kg)	8.1	9.1	7.2
Neutralisation number (mg KOH/kg)	2.0	1.7	1.4
Ca content (ppm)	2300	4600	3700
P content (ppm)	700	1900	1500
S content (ppm)	4900	4300	4200
Zn content (ppm)	900	2100	1600

Each of the following five different artificial ageing procedures was applied to oils A, B and C:

- reference ageing with air (oxidative ageing);
- ageing with the addition of ethanol at low concentration (1% of ethanol in relation to the engine oil volume per day);
- ageing with the addition of ethanol at high concentration (1% of ethanol in relation to the engine oil volume per hour);
- ageing with the addition of acetaldehyde and
- ageing with the addition of acetic acid.

This extensive ageing matrix was applied to find out the impact of each bio-ethanol related compound selected on the oil formulations.

3. Results and discussion

3.1. Artificial ageing of oil A—common engine oil technology

Fig. 2 displays the progression of the most important oil parameters comprising oxidation, neutralization number and total base number during the ageing procedures of oil A. The visual evaluation gave the following results:

- no abnormalities in the appearance of the oil sample during the reference ageing;
- some deposits during the addition of ethanol in low concentration and the development of some particles during addition of ethanol in high concentration;
- development of few particles during addition of acetaldehyde and
- heavy sludge formation during artificial ageing with the addition of acetic acid.

The results demonstrate that the addition of the low concentration of ethanol as well as the addition of acetaldehyde has almost no impact on the progress of oil degradation compared to the reference ageing. The oxidation increases almost linearly to a moderate value of about 8.5 A/cm. The neutralization number slightly drops during the first 48 h due to additive depletion and rises afterwards to a value of 2.5–3 mg KOH/g, which means a rise of 0.5–1 mg KOH/g from the fresh oil. The total base number decreases by about 3 mg KOH/g from the fresh oil value of 8.1 mg KOH/g.

The addition of acetic acid accelerates the ageing process, which is confirmed by higher oxidation of about 12 A/cm after 96 h of artificial ageing, higher neutralization number and slightly lower total base number as well as by heavy sludge formation. The reason for higher oxidation values could be free, not reacted acetic acid in the oil. Special attention was paid to the evaporation of un-reacted acetic acid out of the samples before measurement in order to ensure oxidation values due to base oil oxidation.

Acetic acid may form peracetic acid with peroxides. Peracetic acid is commonly used in organic synthesis as oxidising agent, e.g. used for the epoxidation of alkenes [29]. Higher oxidation values found for acetic acid ageing may be attributed to the oxidation power, resulting in the acceleration of oxidation of oil molecules. Conventional oil analysis is not suitable to confirm this hypothesis but in-depth investigations with high-end analytical methods may give evidence for acetic acid accelerated oil oxidation.

Concerning the mentioned heavy sludge formation during artificial ageing, see details in Section 3.3.

Artificial ageing with the addition of ethanol was carried out at two different concentrations in order to estimate the quantity-dependent effect of ethanol as major compound with respect to

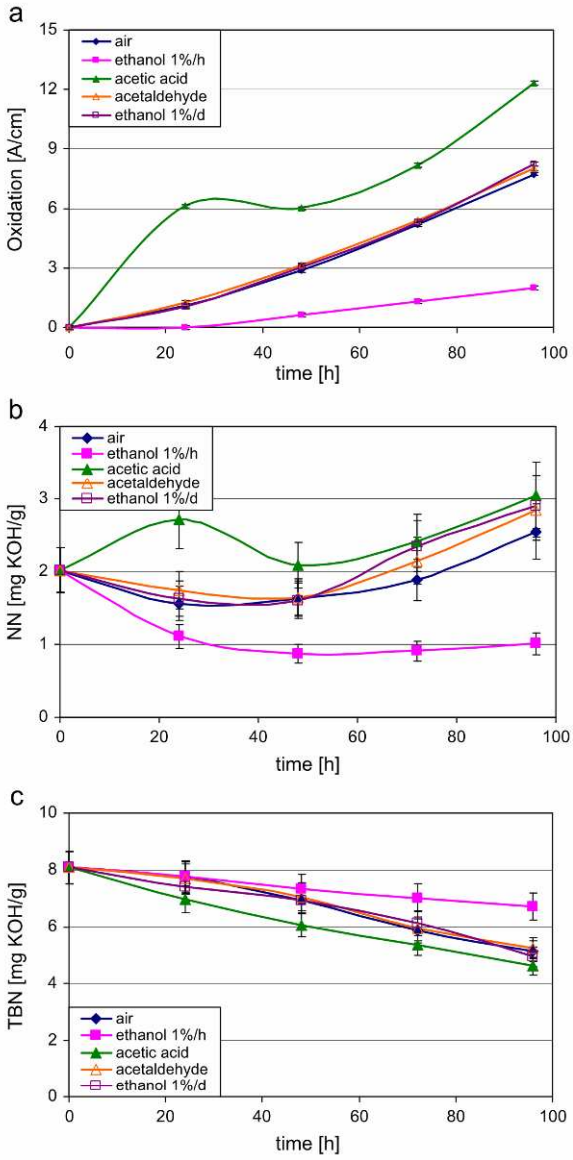

Fig. 2. Oil properties of oil A during artificial ageing: (a) oxidation, (b) neutralisation number, and (c) total base number.

quantities. In particular the impact of the addition of higher ethanol quantities, which apparently slowed down the ageing process, is mentioned. The oxidation value reaches only about a quarter of the oxidation of both the reference ageing and the ageing with low ethanol quantities. The neutralization number drops to about the half of the fresh value within the first 24 h and remains low until the end of the ageing after 96 h. The total base number decreases only half as much as observed during reference ageing. One reason for this ageing behaviour is a possible discharge of volatile ageing products by the evaporation process of larger amounts of liquid added. For total elucidation further investigations have to be done.

These results show that unburnt portions of ethanol as well as acetaldehyde being a representative for partially burnt portions seem to represent only a marginal risk for engine operation in terms of above average changes of typical oil properties at the chosen conditions. On the contrary, acetic acid significantly affects the additive chemistry, e.g. by salt formation. Although the common oil parameters do not show great changes, the sludge formation signifies failure in detergent stability as discussed in Section 3.3. The results suggest that micelles—detergent additives are formed of—are destroyed by acetic acid and subsequently are precipitated.

As expected the addition of the three bio-ethanol related compounds chosen causes different responses of the engine oil in particular demonstrated by the formation of inhomogeneities such as sludge. The responses observed may cause malfunctions in the lubricating system and, in the worst case, engine failure. Therefore an improvement in the oil chemistry with particular regard to the application in bio-fuelled engines is evidently necessary to maintain conventional oil change intervals.

3.2. *Artificial ageing of oils B and C—advanced engine oil technology*

Oils B and C are engine oils based on leading-edge technology with advanced additives in comparison with oil A. They are selected for the demands in bio-fuelled engines and differ in their additive chemistry from each other. Figs. 3 and 4 display the development of the oil parameters during the artificial ageing procedures of oils B and C.

The visual evaluation of oil samples taken from oil B gave the following results:

- no abnormalities in the appearance of the oil during the reference ageing and both artificial ageing procedures with ethanol addition;
- development of very few particles during the artificial ageing with addition of acetaldehyde and
- Formation of sludge above the oil phase already after 24 h of ageing and development of deposits during ageing with the addition of acetic acid

Visual evaluation of the oil samples of oil C showed

- no abnormalities in the appearance of the oil sample during the reference ageing and both artificial ageing procedures with ethanol addition;
- development of very fine sludge particles during artificial ageing with the addition of acetaldehyde and
- artificial ageing with addition of acetic acid showed the formation of fine sludge.

Data obtained for the common oil parameters oxidation, neutralization number and total base number display improved preservation for oil B as well as for oil C compared to oil A.

The oxidation values during the reference ageing and the artificial ageing with the addition of both ethanol concentrations and acetaldehyde for oils B and C do not exceed 3 and 6 A/cm, respectively, which is an indicator for high oxidative stability. Although for both oils the addition of acetic acid causes higher oxidation values, they reach a comparable level after 96 h of artificial ageing as oil A already after 48 h.

Neutralization numbers for both oils and all artificial ageing procedures carried out showed no significant difference between the fresh and the aged oil samples. Exceptions are the artificial ageing of oil B with higher ethanol concentration, which caused the neutralization number to drop to about half the initial value, and the artificial ageing of oil C with acetic acid, where the level rises to 0.5 mg KOH/g. The lowering of the neutralization number during artificial ageing of oil B with the addition of high ethanol concentrations goes along with the results already found for oil A

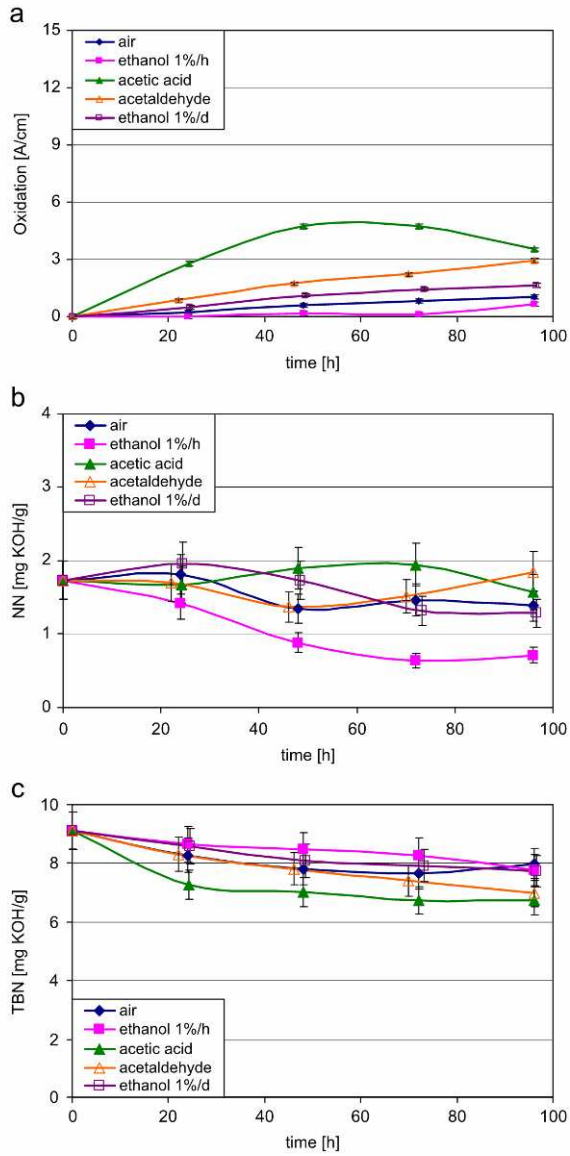

Fig. 3. Oil properties of oil B during artificial ageing: (a) oxidation, (b) neutralisation number, and (c) total base number.

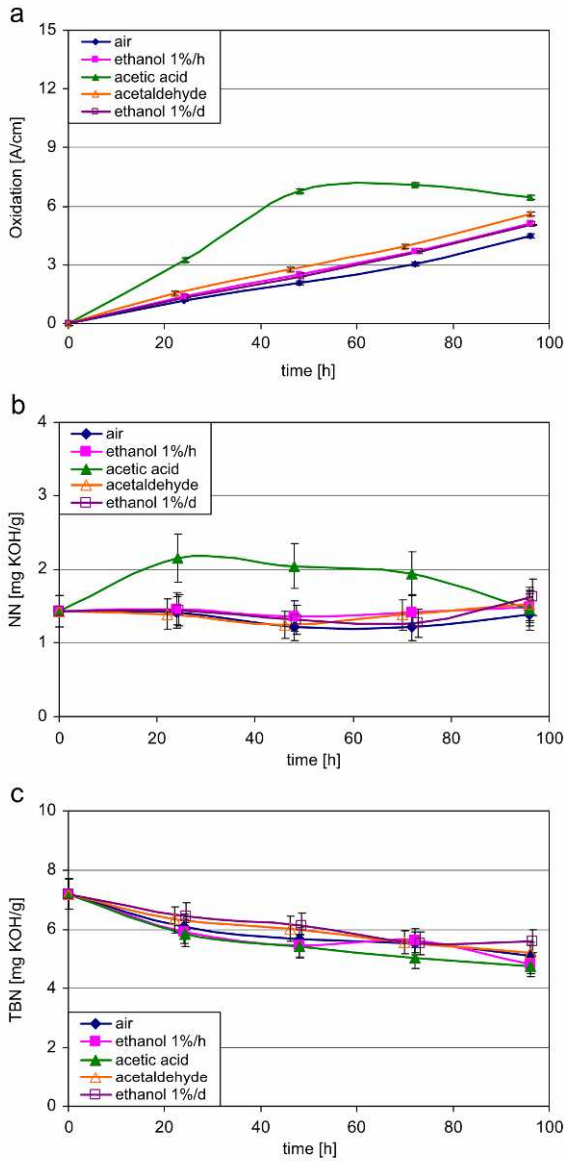

Fig. 4. Oil properties of oil C during artificial ageing: (a) oxidation, (b) neutralisation number, and (c) total base number.

and has the same causes as described. The increasing neutralization number of oil C should not be considered as significant due to the fact that the value after 96 h ageing duration falls to the original value of the fresh oil again.

A marginal drop in total base number of about 1–1.5 mg KOH/g has been usually found on artificial ageing of oils B and C, which signifies high stability against the chosen compounds. One exception is the ageing of oil B with acetic acid, where the total base number decreases to about 7 mg KOH/g in the first 24 h, which is a drop of approximately 2 mg KOH/g, and afterwards remains stable until the end of the artificial ageing process. Even in this case the loss of total base number is not dramatic and should not be considered harmful for use.

Higher amounts of ethanol exerted a positive effect on the ageing behaviour of oil B but not as much as for oil A. It is expressed in lower neutralization numbers. On the other hand oil C does not show any sensitivity to higher quantities of ethanol added, which is attributed to a lower capacity of oil C for the uptake of ethanol compared to the other oils.

3.3. Sludge investigation

The formation of sludge caused by oil degradation is a widespread and commonly known problem. It is one of the main reasons for failures in lubricated systems during operation and, in the worst case, for machine breakdown. Therefore a low

capability for sludge formation is very important for the applicability of oils in general.

The results of artificial ageing as discussed above show that bio-ethanol related compounds cause deposit formation under certain conditions. This knowledge obtained from lab-based methods can be used to reduce the formation of sludge and deposits in the field by optimisation of lubricant formulations with special regard to the introduced compounds to be expected. Further investigations have to be made concerning measurements of size, density and distribution of particles as well as their surface properties, which are important factors for sludge formation.

3.3.1. Impact of acetaldehyde

The effect of acetaldehyde on the morphology and the composition of sludge formed during artificial ageing of oils B and C was investigated by SEM-EDX. Fig. 5 shows representative images.

Sludge formation was very low compared to artificial ageing procedures with acetic acid, especially with oil B, which is supported by the fact that only very few particles were found. Deposits formed during artificial ageing with acetaldehyde are very fine and dark, almost black. They appear globular and porous, partly even hollow, for both oils. Due to the sampling for condition monitoring, the gravimetrical quantification of total sludge at the end of the artificial ageing duration was not possible.

Elemental analysis by SEM-EDX is summarised in Fig. 6. Calcium, phosphor, sulphur and zinc are the elements found in the sludge of both oils, which indicate their origin in the oil additives—detergents and zinc dialkyl dithiophosphate (ZDDP) as anti-wear additive.

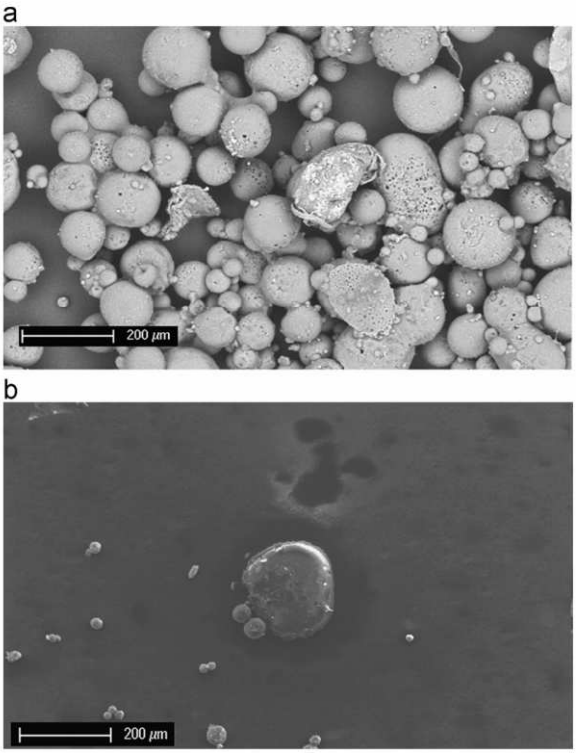

Fig. 5. SEM images of sludge formed during acetaldehyde ageing of (a) oil B and (b) oil C.

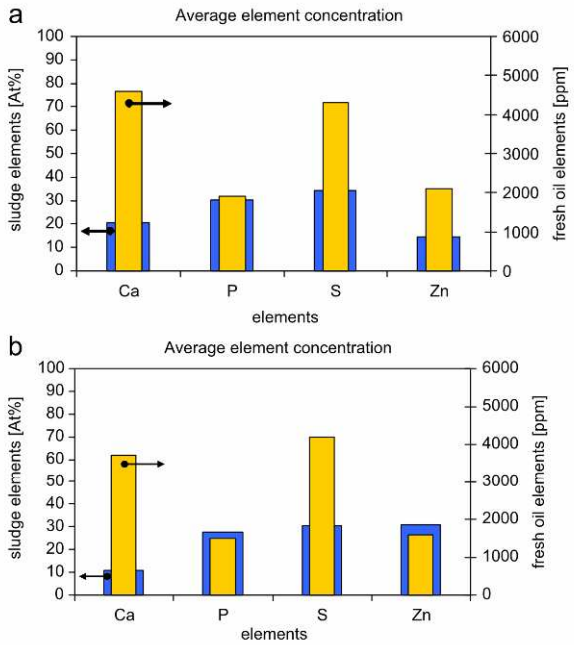

Fig. 6. Elemental analysis of sludge formed during ageing with acetaldehyde, comparison of contents of layer/particle-forming elements in sludge and fresh oil: (a) oil B and (b) oil C. Note that carbon and oxygen are not quantified but exceed 90 at% in all cases by EDX.

It is remarkable that calcium was identified in rather low concentrations in spite of high calcium content in the fresh oil. Conversely disproportional high amounts of phosphor, sulphur and zinc, all ingredients of anti-wear additives were found in the sludge. In contrast to the results for acetic acid, these findings indicate the negative effect of acetaldehyde on anti-wear additives whereas detergents are only slightly affected.

3.3.2. Impact of acetic acid

The morphology and the composition of sludge formed on artificial ageing with acetic acid were studied under two different ageing conditions: artificial ageing procedures were carried out under (a) 'conventional conditions' with a liquid dosage of 0.1%/h for a duration of 96 h and under (b) 'harsh conditions' whereas acetic acid was added at a dosage of 0.5%/h for a duration of 24 h.

SEM-EDX investigations show different morphologies depending on the artificial ageing conditions as depicted in Fig. 7 for oil C. 'Conventional conditions' produced only few particles of hollow and spherical structures with a size of up to 100 µm. On the contrary, 'harsh conditions' cause crude voluminous chunks agglomerated out of particles without defined shape.

SEM-EDX analysis of the particles indicates the elements involved in the particle composition. Fig. 8 compares the elemental compositions resulting from artificial ageing under 'conventional and harsh conditions' regarding the respective fresh oil metal contents in the fresh oil C. Calcium, phosphor, sulphur and zinc are the elements found in the sludge under both conditions. Calcium, an important ingredient in detergents and an indicator for the total base number [30], is the main component with more than 60 at% in comparison with the other elements analysed. Sulphur shows remarkable results: it is the main element in fresh oil C but can only be found in small amounts in the sludge. These results of low sulphur contents in sludge correspond to findings of

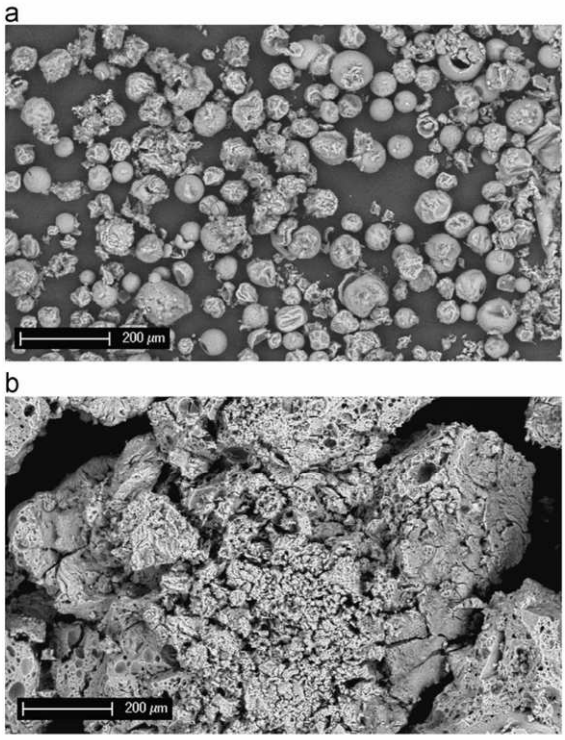

Fig. 7. SEM images of sludge formed during acetic acid ageing at different ageing conditions of oil C: (a) depicts particles formed under "conventional" conditions and (b) shows particles formed under "harsh" conditions.

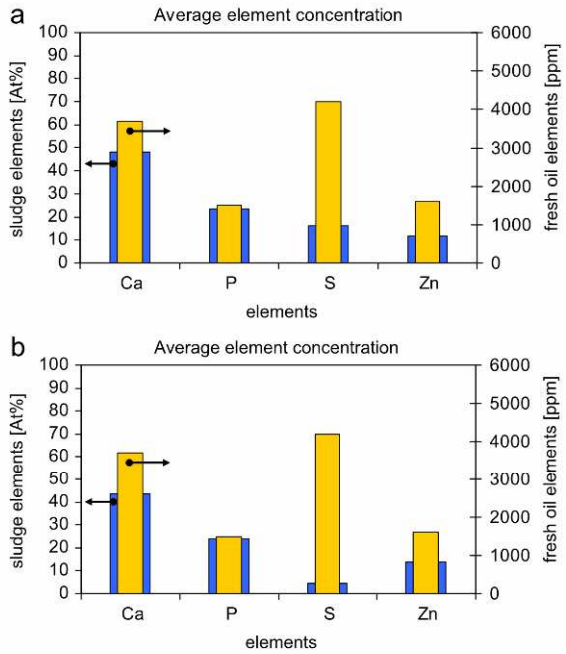

Fig. 8. Elemental analysis of sludge formed during ageing with acetic acid, comparison of contents of layer/particle-forming elements in sludge and fresh oil C: (a) under conventional conditions and (b) under harsh conditions. Note that carbon and oxygen are not quantified but exceed 90 at% in all cases by EDX.

other artificial ageing procedures, e.g. artificial ageing of oil A with the addition of acetic acid.

The knowledge gained suggests that acetic acid in engine oils caused preferably detergent depletion in the liquid accompanied by the destruction of the micellar structure [30] but has no significant effects on anti-wear additives under the conditions chosen.

4. Conclusions

The aim of this study was to develop a novel setup of artificial ageing, which can generate data for the simulation of ageing conditions in bio-fuelled engines. The performance of the method developed was illustrated by the example of engine oil formulations optimised for the use in vehicles run with ethanol containing fuels. Artificial ageing was realised by the addition of compounds originating from ethanol to the oil sample. Furthermore, the potential of this novel lab-based method should be demonstrated by a stepwise optimisation of engine oil formulations in terms of stability against strains prevailed in bio-fuelled engines.

The following characteristics of the novel lab-based artificial ageing method have been achieved:

- A comparison of the reference ageing methods carried out only with air according to currently used standard methods and the artificial ageing with bio-ethanol related compounds showed clearly the impact of the applied fuel components on the ageing characteristics of the engine oils.
- It is a pronounced short-term method to investigate the long-term behaviour of engine oils enabling the pre-selection thereof according to their performance under specially chosen conditions.
- A clear differentiation in the performance between different oil formulations concerning their stability against chemical and oxidative degradation is enabled by consecutive condition monitoring.
- A flexible method is created, which affords the opportunity to adapt ageing conditions to requested engine conditions by the variation of the ageing parameters.

Based on the results from the investigation of ethanol and its combustion products, several benefits of the novel artificial ageing method can be stated:

- The impact of various bio-ethanol related compounds on the ageing behaviour of oils can be investigated by lab-based artificial ageing and simulating specific real-life conditions.
- Each compound can be studied independently from other influences, hence avoiding interferences, which would make interpretations difficult. The gained knowledge can be used for performing further high-end analysis, e.g. mass spectrometry of aged oil samples.
- It was shown that ethanol and acetaldehyde possess only marginal influence on the ageing behaviour of the engine oils in terms of common oil condition parameters whereas acetic acid advances oxidation processes and induces considerable sludge formation.

For the development of new oil formulations, following conveniences can now be provided:

- Possibility of a stepwise improvement of oil technology was shown by means of the novel artificial ageing method.

- Suitability of formulations and the long-term effectiveness of oil components for the applications intended can be evaluated in a cost and time efficient way prior to expensive engine bench tests.

As a future prospect, further investigations are planned comprising high-end analysis of oil samples from artificial ageing. Here, modern desorption/ionisation mass spectrometry is proposed to elucidate ageing mechanisms on the molecular level. Particle size distribution and composition of the washed particles of the sludge are of interest too.

Based on the outlined strategy and involved methods an integrated investigation of the effect of the oil condition on bulk oil properties as well as interaction characteristics should be performed and a deep knowledge on the molecular level should be gained.

Acknowledgements

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2.2. Impact of engine oil degradation on wear and corrosion caused by acetic acid evaluated by chassis dynamometer bench test

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Impact of engine oil degradation on wear and corrosion caused by acetic acid evaluated by chassis dynamometer bench tests

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ABSTRACT

The impact of acetic acid as partial combustion product of ethanol, a bio-derived component in gasoline, on the performance of two engine oils regarding their stability and corrosion potential towards engine parts was assessed. Consequently, oils evaluated in laboratory for their stability were subjected to a chassis dynamometer bench test for examination under more realistic conditions. In addition to reference runs, bench tests were performed with addition of acetic acid to the oil. Oil condition monitoring enabled the differentiation between runs with and without addition of acid concerning the oil parameters Total Base Number and Neutralisation Number. Moreover, interaction of the oils with acetic acid could be differentiated attributed to different oil formulations. Optical emission spectroscopy of oil samples proved the corrosion potential towards iron and copper when adding acetic acid although this contamination has been largely evaporated during the bench tests. However, failure assessment by scanning electron microscopy of used parts demounted from the vehicle after the bench tests showed no significant signs of mechanical wear or corrosion giving evidence for material loss in nano- to micro-scale. As corroboration of these findings, static corrosion experiments were performed in the laboratory with good correlation to results obtained from the bench test.

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1. Introduction

In the last decades, an increasing awareness towards the use of bio-fuels has been observed. The reasons for the application of this type of liquid fuels are very divergent. Particular environmental issues are coming up due to the intensive use of fossil fuels like pollution and the depletion of resources, climate change and high CO_2 emissions combined with global warming. These facts are assumed to cause environmental disasters, e.g. heavy rains, floods and frequent hurricanes. Economic considerations comprise the reduction of the dependency on fossil fuels in the transport sector, the valorisation of new employment opportunities, and the strengthening of rural economies. The growing fuel consumption due to the growing number of diesel engine powered heavy-duty haulage trucks and city buses, agricultural tractors and self-propelled machines as well as personal light-duty cars results in high market fuel prices and a demand of mineral fuels growing faster than their production capabilities [1–4].

These concerns were taken up by legislation. In 2009, the European Union released the directive 2009/28/EC [5], to prescribe and regulate the use of renewable energy within the EU member states. There it is specified, that until the year 2020, 20% of the total energy consumption should come from renewable sources. In the transportation sector, these are mainly fatty acid methyl esters (FAME) as bio-components in diesel fuels and in the case of gasoline ethanol produced from biomass is commonly used. Especially ethanol possesses various benefits compared to conventional gasoline, e.g. it has non-petroleum origin, it can be used as powerful fuel oxygenate and possesses octane-boosting properties [4].

In contrast to this, ethanol exhibits some disadvantages, e.g. concerning material compatibility due to corrosive impact which it can have on automotive parts. Surisetty et al. stated that the main reasons for corrosion issues in the presence of alcohols in fuels are the increased water content due to hygroscopy of ethanol and partly the presence of organic acids. Besides, alcohols are polar solvents and, hence, corrosive to metal engine parts [6]. Baena et al. describe the different types of corrosion that can be caused by ethanol. They carried out immersion tests with different metallic materials commonly used in the automotive industry in a blend with 20% bio-ethanol in gasoline (E20) and found that copper and carbon steel had the highest

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tendency towards corrosion and therefore were not recommended for applications with direct E20 contact [7]. Krüger et al. determined the corrosion potential of different aluminium alloys in ethanol blended gasoline by immersion and polarisation tests at various temperatures. They stated that dry corrosion is strongly dependent on temperature and water content of the mixtures. In addition, they showed that temperatures close to the boiling point of ethanol provoke heavy corrosion [8].

In order to determine the corrosion potential of petroleum products, various standards are currently used. Thereby, the corrosive impact on different metals, usually copper [9,10] or steel in combination with water [11] is determined by immersing the test specimen into the respective liquid at elevated temperatures. Other standards [12,13] evaluate the corrosiveness to silver of automotive spark-ignition engine fuels with comparable methods. But all conventional standards have in common that only the impact of model metals is assessed. This represents a severe disadvantage concerning the goal of a realistic simulation of conditions in the engine, where diverse alloys and materials are in use. Therefore, the need for novel adapted corrosion experiments is growing to determine the corrosion potential of fuels as well as lubricating oils taking account for current and future fuel qualities.

In order to investigate the impact of ethanol as bio-derived component in gasoline fuels on the performance of three selected engine oils regarding their stability, a novel artificial alteration method in the laboratory was recently proposed for the simulation of conditions in bio-fuelled engines. Thereby, ethanol as well as its partial combustion products acetaldehyde and acetic acid were added continuously to different engine oils kept at elevated temperatures and brought in contact with dried air. In doing so, a pre-selection of oils for the usage in bio-fuelled combustion engines and advancement in engine oil technology was enabled [14].

In a consecutive step of the study, the engine oils evaluated in the laboratory for their stability were further subjected to a chassis dynamometer bench test to examine them under real engine conditions. As an overall contemplation, a chemometric data evaluation was done comparing oil samples altered in the laboratory experiments with samples from the engine [15].

This paper presents results from oil condition monitoring during the chassis dynamometer bench tests. The main focus was laid on the interactions of the oil with bearing surfaces. The corrosion potential of two engine oils (15W-40 and 5W-30) was evaluated by failure assessment of original parts of the vehicle operated in the bench test as well as by static corrosion experiments carried out in the laboratory.

2. Experimental

2.1. Chassis dynamometer bench tests

2.1.1. Procedure description

The chassis dynamometer test bench was the device of choice in order to investigate the influence of ethanol as well as its partial combustion product acetic acid on the engine oil deterioration under real conditions. For this study, a 4 wheel test bench with two driven axles in a climatic chamber was chosen designed for two as well as four wheeled vehicles. It exhibited a driving and braking power of 90 kW, a maximum speed of 160 km/h, and minimum gyrating mass of 3500 kg. The climatic chamber possessed an airflow capacity of 80,000 m^3/h, a refrigerating capacity of 100 kW and a temperature minimum of −35 °C.

In the course of the scientific work, specific driving situations were simulated in a conventional passenger car equipped with a modern gasoline direct injection engine with supercharging. It comprised a downsizing concept for obtaining high engine loads with 1390 cm^3 displacement and 125 kW output at 6000 min^{-1}.

The vehicle was driven with conventional super unleaded gasoline available on the market of 2010 with a Research Octane Number of 95. It contained 0.3 vol% of ethanol and 9.8 vol% of ethyl tert-butyl ether (ETBE), resulting in a total amount of ethanol in the bio-derived components of 4.7% as prescribed in the standard DIN EN 228 of November 2008 [16]. Therein, a maximum ethanol concentration of 5 vol% is specified.

In order to simulate severe driving conditions, a special driving cycle was designed consisting of two different steady state operation points which were applied in alternating manner: the first one, operation point 1, had low road velocity (50 km/h), low rotational speed (2000 rpm), as well as low load (250 N). At operation point 2, the car was driven with increased operating parameters, i.e. a road velocity of 80 km/h, a rotational speed of 3000 rpm, and a load of 750 N. In the course of one driving cycle, operation point 1 was applied for 30 min, followed by 1 h of operation point 2. The session was closed by driving operation point 1 for 1 h. The cycle was performed two times per day producing a total driving distance of about 312 km per day. The procedure is also presented in [17].

Besides using these conventional driving conditions, the attempt was made to transfer artificial alteration acceleration from the laboratory to the engine system. By this means, it was considered to find correlations between the real application and artificial alterations carried out in the laboratory concerning engine oil deterioration mechanisms induced by ethanol and partial combustion products thereof within a reasonable time frame.

The detailed novel laboratory procedure of artificial oil alteration is also described in [14]. This method comprised an oil sample (300 g) placed in a round bottomed three-neck glass flask (500 mL) kept at a defined temperature (160 °C) in a heating oil bath. Dried air (10 L/h), which was adjusted by a flow controller, was bubbled through the oil via a glass tube. For the simulation of the influence of bio-components in the fuel on the engine oil performance, acetic acid was added continuously to the oil throughout the whole experiment duration via an additionally equipped Teflon tube, in total 0.1% per hour related to oil volume. In doing so, an exposure of the engine oil to special conditions was enabled. In this study it was shown, that ethanol as well as acetaldehyde possess only marginal effect on the alteration characteristics of engine oils whereas acetic acid exhibited a significant negative impact on the engine oil emphasised by decreased oil stability and heavy sludge formation.

According to these findings, acetic acid in the form of glacial acetic acid was chosen to be also added continuously to the engine oil during the chassis dynamometer tests. In doing so, the oil was pumped out of the oil pan of the passenger car via a bypass system to the inlet of an automatic titration device. There, acetic acid was added in small portions to the oil resulting in a total amount of 0.5% acetic acid per day, i.e. 5 h of operation, in relation to the engine oil filling capacity of 4.5 L, similar to the artificial alteration in the laboratory. Subsequently, the contaminated oil was pumped back to the oil sump of the car. A schematic representation of this pumping cycle is shown in [15].

For interpretation of the data obtained, the chassis dynamometer bench tests with addition of acetic acid were compared to reference runs without the addition of this contamination.

2.1.2. Engine oils

For artificial alteration in the laboratory, three fully formulated engine oils were chosen representing a consecutive development in engine oil technology. Oil A with group I mineral base oil and viscosity grade SAE 15W-40 was representative for the common engine oil technology currently available in the market. Based on the degradation characteristics of this oil during artificial alteration the improved

formulation of oil B [14] (data not shown) with viscosity grade SAE 5W-40 was generated resulting in the subsequent development of oil C with the viscosity grade SAE 5W-30 also with group III hydrocrack base oil. The main physico-chemical parameters of the applied oils are displayed in Table 1.

On the chassis dynamometer bench test, oil A with the lowest performance during artificial alteration in the laboratory and oil C which showed the highest stability during artificial alteration were assessed. These two engine oils were selected in order to screen the performance range of oils with different technologies.

2.1.3. Oil condition monitoring

During the bench test runs, periodical sampling was carried out after the second driving cycle in the end of each day. A teflon tube was inserted into the oil sump through the oil dipstick tube. The oil samples were taken after 20 h, 40 h, 60 h, and at the end of operating time and used for continuous oil condition monitoring to investigate the oil stability over time. Attention was paid to take representative samples with the same composition compared to the oil in the sump. Therefore, the oil sample was investigated with the abdication of any preparatory step such as additional evaporation of free, un-reacted acetic acid, in order to avoid loss of volatile alteration products, in particular acetic acid.

2.1.3.1. Conventional oil parameters. In order to elucidate the influence of acetic acid as partial combustion product on the performance of the engine oil, conventional oil parameters related to acid-base reactions were monitored: measurement of the base reserve (Total Base Number, TBN) was carried out by potentiometric perchloric titration according to a standard method DIN ISO 3771 [18]. TBN is given as the amount of perchloric acid in equivalent mg of potassium hydroxide used for the neutralisation of all basic components in 1 g of oil sample. According to the standard method DIN 51558 [19], the neutralisation number (NN) was quantified as the amount of base needed to neutralise all acid components in an aliquot of 1 g oil sample.

2.1.3.2. Supplementary analyses. Additional to conventional oil parameters, the condition of the engine concerning corrosion and wear was characterised by the quantification of typical elements in the oil such as iron, copper, and aluminium.

All elemental analyses were carried out by optical emission spectroscopy equipped with inductively coupled plasma (ICP-OES) (Varian Vista MPX with axial plasma torch, Varian Analytical Instruments, Melbourne, Australia) after microwave treatment of the oils with nitric acid.

2.2. Failure assessment

The condition of the engine concerning wear and corrosion after the chassis dynamometer bench tests was described starting with a visual evaluation of engine parts removed from the operated passenger car and thoroughly rinsed with petroleum ether. This procedure was followed by scanning electron microscopy (SEM). Therefore, a scanning electron microscope Philips XL30 ESEM-FEG coupled with energy dispersive X-Ray analysis device (SEM–EDX) (Philips Electron Optics, Amsterdam, The Netherlands) was utilised. Images were obtained applying two methods; surface properties at high lateral resolution were investigated by a secondary electron detector (SE). Besides, a backscattered electron detector (BSE) produced images with elemental contrast. In addition to this, the elemental compositions of the engine parts' surfaces were determined using EDX (Genesis system with SUTW Window, EDAX).

For failure assessment the small end bearing, the big end bearing and the piston pin of the same piston were selected.

2.3. Laboratory corrosion experiments

For evaluating the corrosion potential of the oils sampled during the chassis dynamometer bench tests, static corrosion experiments in the laboratory were carried out. Unused genuine parts of the passenger car, driven on the test bench, were stored in 5.5 g of used oil crimped in 8.5 mL glass vials at 160 °C in an oven. The glass vials were sealed in order to prohibit oxidation processes due to contact with oxygen from the atmosphere.

As genuine parts, the small end bearing as well as the big end bearing from a vehicle of the type 1K/ABBLGX0/FA6FD62E022N4 0GGN1, the same as operated on the bench test, were reordered, cut into uniform pieces (small end bearing: 10 mm × 30 mm; big end bearing: 8 mm × 26 mm) and cleaned with toluene and petroleum ether. As respective used oils, aliquots sampled after 40 hof operation on the dynamometer (half of the experimental duration) were applied. The amount of oil was selected to keep the volume of the gas phase above the oil at a minimum in order to avoid evaporation of volatile components to the gas phase above the oil surface.

Corrosiveness assessment was done via detection of typical material elements in the oil phase. These were copper and iron for the small end bearing and aluminium and iron for the big end bearing, respectively. Small aliquots of oil were taken from the vial after 72, 144, and 240 h of storage and analysed by ICP-OES after microwave treatment.

In addition, the appearance of the genuine parts after 240 h of corrosion experiments was evaluated visually after careful cleaning with petroleum ether. The surface of the specimens was investigated by the means of SEM, the elemental composition of the sample surface and deposits was determined by EDX.

3. Results and discussion

3.1. Chassis dynamometer bench test

3.1.1. Oil condition monitoring

Fig. 1 shows the development of the conventional oil parameters TBN and NN of oils A and C during the chassis dynamometer bench

Table 1
Physico-chemical properties of engine oils A and C (see also [14]).

Oil parameter	Unit	Method	Oil A	Oil C
Kinematic viscosity at 40 °C	mm^2/s	ASTM D 7042	101	70.5
Kinematic viscosity at 100 °C	mm^2/s		13.7	11.8
Density at 15 °C	g/cm^3		0.88	0.85
Viscosity index	–	ASTM D2270	135	164
Total base number	mg KOH/kg	DIN ISO 3771	8.1	7.2
Neutralisation number	mg KOH/kg	DIN 51558	2.0	1.4
Ca content	ppm	In-house method (see 2.1.3.2.)	2300	1900
P content	ppm		700	700
S content	ppm		4900	2100
Zn content	ppm		900	800

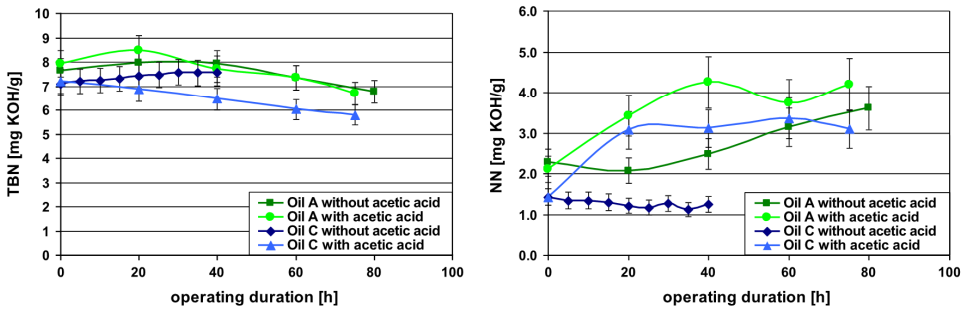

Fig. 1. Conventional oil parameters of oils A and C during chassis dynamometer bench test. *Note*: lines between data points only serve for visualization; they do not compulsorily reflect the real progress.

tests. The reference run of oil C without contamination exhibited only little degradation confirmed by TBN, NN, and elements. Thus, it was aborted after 40 h of operating duration. It can be estimated by the stability of the oil performance in the first 40 h that oil C behaves quite similar to oil A during the reference run.

The TBN shows a slight increase in the first 40 h of the experiment followed by a constant decrease of about 1 to 2 mg KOH/g for all bench test runs. An exception is the run with the addition of acetic acid of oil C where a continuous decrease of 1.3 mg KOH/g is observed from the beginning throughout the whole operating duration. The increase in TBN values in the beginning of several runs can be explained by basic substances produced and brought in the oil during engine operation. In-depth investigation, for example by mass spectrometry, may give detailed information about this hypothesis.

The NN provides a quite good differentiation between runs with and without contamination. In the case of reference runs without contamination, a slight decrease – inversely to the increase in TBN – was found followed by a continuous increase. On the contrary, during runs with the addition of acetic acid a strong increase of NN occurs during the first 20 h for both oils A and C. Afterwards, the NN almost stays stable during the run with oil C whereas the NN of oil A increases until 40 h of operating duration followed by a decrease, which can be ascribed to the refill of a small amount of fresh oil to the car which was necessary for further oil sampling. In the end of the experiment, the level of the NN after 40 operation hours is reached again. The elevated levels of NN in oil samples from bench test runs with addition of acetic acid can be ascribed at the one hand to the build-up of acidic degradation products formed during engine operation and on the other hand to free, not reacted acetic acid.

Acetic acid was added in order to reach a total concentration of 0.5% acetic acid per day in relation to the engine oil filling capacity, which means, that the treat rate was 4.5 mL of acid per operation hour. This addition would – provided that the whole amount of acid has completely reacted with base reserve – provoke a decrease in TBN of approximately 1.1 mg KOH/g per hour in the case of oil A and 1.2 mg KOH/g per hour in the case of oil C. Or in the case that acetic acid is neither consumed by base reserve nor exhausted, an increase of NN in the same order would occur.

For the estimation of acetic acid conversion in the engine oil, it was assumed that the impact of acetic acid can be described by the difference of TBN and NN between runs with and without acetic acid. In the case of oil A, no considerable difference of TBN and NN, respectively, could be found at the end of the runs. These findings suggest that 1) the detergent providing base reserve did not significantly react with acetic acid, i.e. decrease of TBN, and 2) unreacted acetic acid did not substantially accumulate in the engine oil, i.e. increase of NN. By contrast in oil C, acetic acid resulted in a TBN decrease of about 1.1 mg KOH/g and an NN increase of about 1.9 mg KOH/g compared to the run without acetic acid after 40 h of operation. Thus, TBN and NN values of the oil samples exhibited only a marginal decrease of TBN and a marginal increase of NN in relation to the total quantity of acetic acid added. This suggests that only about 3% of the added acetic acid has reacted and accordingly about 5% is existent as unreacted acetic acid. The rest has evaporated by the thermal conditions supported by oil agitation by moving engine parts. These facts indicate that if acetic acid is produced as partial combustion product during the operation of a vehicle driven with a portion of bio-ethanol in the gasoline, the acid will most likely be evaporated easily, hence causing rather low corrosion potential in the oil and consequently a low risk of damage in the engine.

3.1.2. Supplementary analyses

Fig. 2 shows the development of the wear element content in the oil during engine operation on the chassis dynamometer test bench. Obviously, aluminium parts in the engine are not affected from corrosive or abrasive wear, proved by very low and constant concentrations of aluminium in the oil throughout the whole bench test runs. This is independent whether acetic acid was added or not as well as from the respective oil applied.

In addition, it can be stated, that almost no wear occurs during the reference runs without addition of contamination to both oils, indicated by very low and constant concentrations of iron and copper.

On the contrary, elevated concentrations of copper as well as of iron were measured during engine operation with the addition of acetic acid. The copper concentration slowly rises up to 16 ppm but is not affected by the quality of the oils. Both runs, with common oil A and with advanced oil C, respectively, produce the same amount of copper in the oil. But the iron accumulation seems to be highly dependent on the oil chemistry. Whereas an iron concentration of 42 ppm was measured in the end of an run with oil A, the run with oil C caused an iron enhancement in the oil up to 62 ppm, which is an increase of almost 50% related to oil A.

3.2. Failure assessment

3.2.1. Small end bearing

The visual appearance of the small end bearing is shown in Fig. 3a. The sliding surface of the tribo-contact exhibits a channel texture. SEM–EDX investigations proved the composition thereof to be a copper layer with tin inclusions on a steel substrate protected itself by a thin tin layer. Fig. 3b shows exemplarily a SEM image thereof with the magnification of 500. The whole inner surface depicting the tribo-contact of the bearing appeared consistent and free of serious wear.

Organic deposits were found especially in the deepening of the channels, visible as darker stripes, mainly consisting of carbon and oxygen with the typical oil additive elements phosphor, calcium and sulphur. Particles with predominately organic composition were found

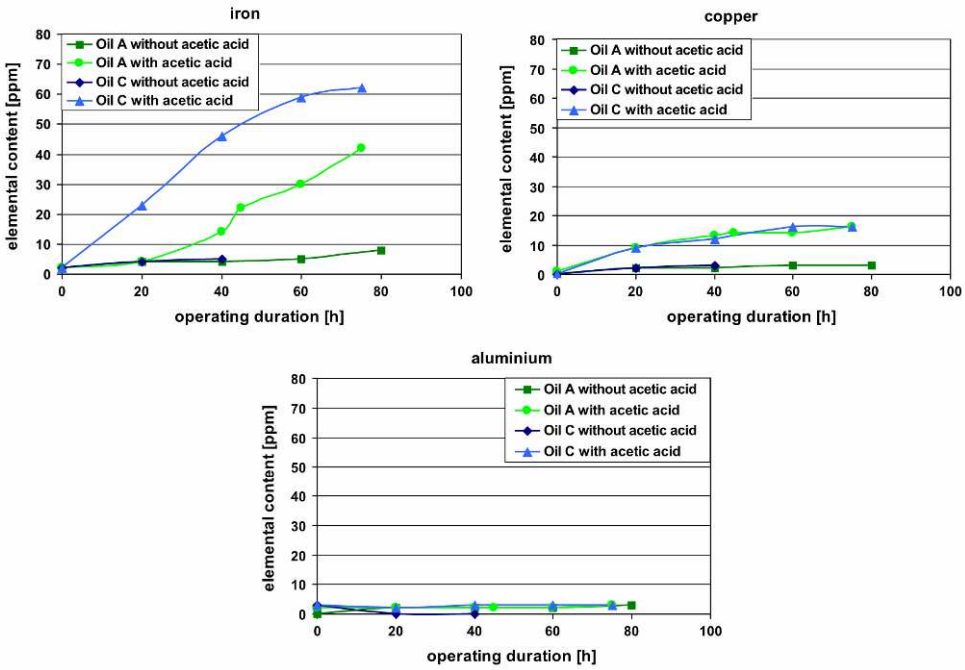

Fig. 2. Content of elements related to material loss found in the oil samples during chassis dynamometer bench test. *Note*: lines between data points only serve for visualization; they do not compulsorily reflect the real progress.

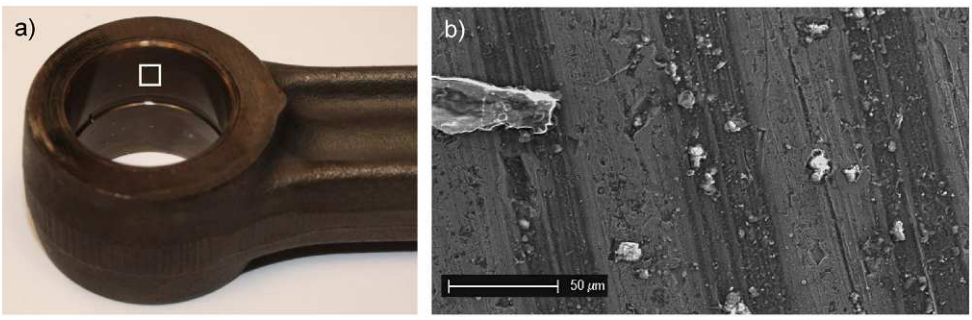

Fig. 3. Small end bearing (white square marks area of SEM investigation): (a) photograph (bearing still installed in the piston rod); (b) SEM image of the surface with channel texture.

loose on or pressed into small holes of the surface, shown as light grey spots.

Significant signs of corrosion could not be found.

3.2.2. Big end bearing

Fig. 4a shows the visual appearance of the upper half-shell of the big end bearing attached to the piston rod. The composition was determined by SEM–EDX to be an aluminium layer with tin and very few nickel inclusions on a steel substrate. In addition, a banded surface structure was found with alternating rough and smooth stripes in direction of rotation, see Fig. 4b and c.

The surface of the used bearing appeared to be slightly rougher with a more pronounced banded structure than the fresh bearing with a very smooth and only marginally structured surface (see Fig. 4b and c).

Spots of pronounced organic deposits were found on the used bearing surface, representatively depicted in Fig. 5. EDX proved the main composition to be carbon and oxygen with traces of phosphor, sulphur, calcium, as well as magnesium, all originating from the engine oil. These spots accumulated preferably at the rough parts of the banded structure suggesting that this texture promotes the deposition of organic compounds.

3.2.3. Piston pin

The visual appearance of the steel piston pin is shown in Fig. 6a. The piston pin exhibits almost no deposits on the locations of direct friction contact, where a blank steel surface with slight wear scars in the direction of rotation can be found, clearly shown in Fig. 6b. In contrast to this, thick organic layers were found on locations without direct tribo-contact, depicted in Fig. 6c and d. This layer is crusty and seems to grow on the blank surface which

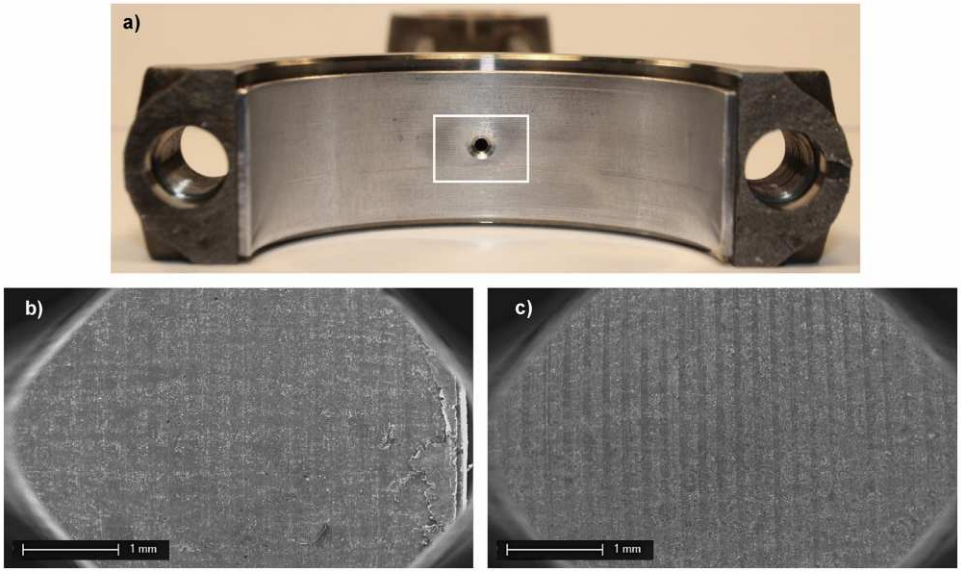

Fig. 4. Big end bearing (white square marks area of SEM investigation): (a) photograph of the upper half-shell (still installed in the piston rod); (b) SEM image of the new bearing surface; (c) SEM image of the used bearing surface.

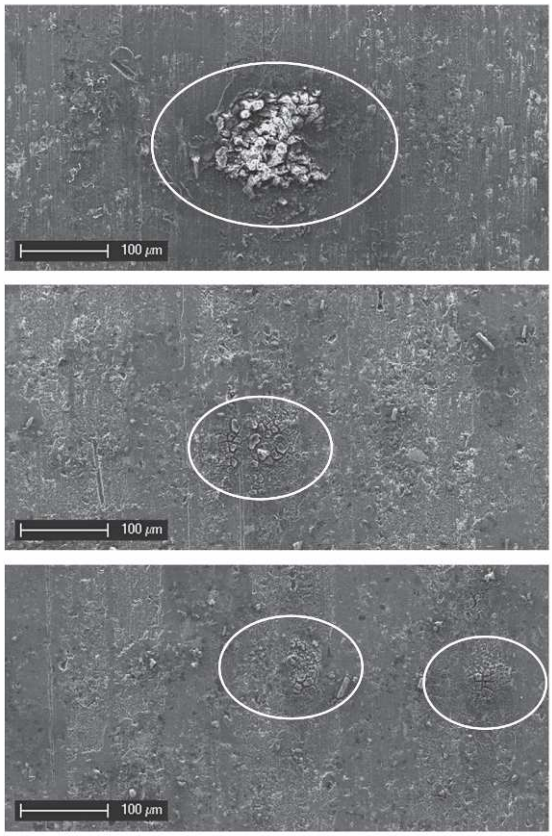

Fig. 5. SEM image of pronounced organic deposits on different locations on the big end bearing surface (accentuated by white circles).

can partly be seen in small openings of the deposit. Small cracks in the organic layer, accentuated by white circles in Fig. 6d, suggest that it is rather loosely bound onto the surface instead of forming a compact coating and therefore can be easily removed, e.g. by rubbing. As consequence of these findings a mechanism for deposit formation with alternating occurrence of build-up and removal can be proposed. Locations with very thin layer of deposit were also found, which are "copying" the texture of the blank surface, see Fig. 6e, still depicting wear scars of the steel specimen. This supports the hypothesis of the proposed deposit formation and decomposition mechanism.

By SEM–EDX the main components of this layer were identified to be carbon and oxygen (together up to 80 at%) with admixture of the typical oil additive elements calcium (detergents), sulphur, phosphor, and zinc (all antiwear additives).

3.3. Laboratory corrosion experiments

Fig. 7 shows the development of selected element contents of typical genuine part elements in the oil during the corrosion experiments with small end bearings. It was found that both the inner coating and the steel substrate were corrosively affected during exposure to certain oils indicated by the presence of elevated concentrations of copper as well as iron in the oil phase.

Especially concerning iron, the impact of acetic acid is considerable. Oils from runs with the addition of acetic acid showed high amounts of iron whereas the iron concentration in oils from reference runs stayed almost below 5 ppm. This leads to the conclusion, that oils from the reference runs exhibit almost no corrosion potential while oils exposed to acetic acid during operation possess high corrosion potential towards iron-containing components. An important fact thereby is the high dependence of this phenomenon on the oil quality. Whilst both oils exhibited very similar behaviour – a steep rise – in the first three days of the experiment, the increase of the iron concentration in the advanced technology oil C seems to slow down in the next 168 h coming to a level of ~350 ppm. This is approximately 25% less than the iron concentration in common quality oil A, in which the iron

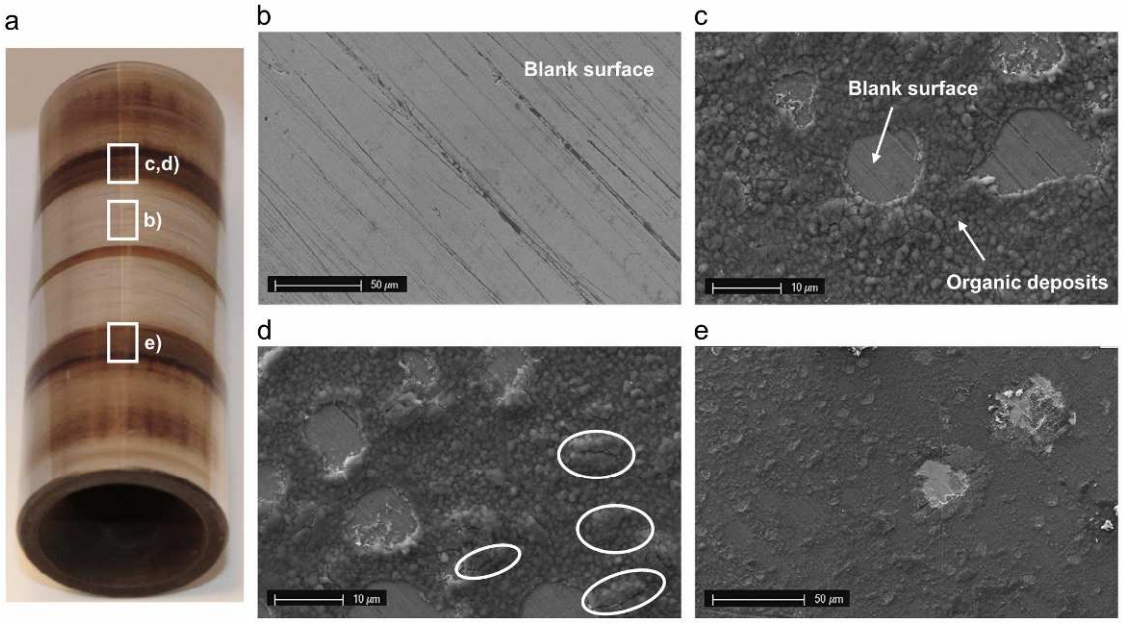

Fig. 6. Piston pin (white squares mark area of SEM investigation, respectively): (a) photograph; (b) SEM image of the blank surface in locations of friction contact; (c) SEM image of organic deposits in locations of no friction contact; (d) SEM image of organic deposits in locations of no friction contact (small cracks in the layer accentuated by white circles); (e) SEM image of organic deposits in locations of no friction contact (wear scars depicted in very thin layer).

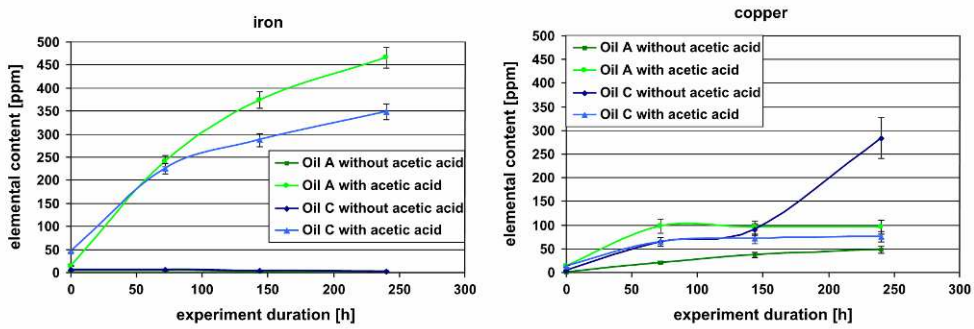

Fig. 7. Content of elements during laboratory corrosion experiments of the small end bearing. *Note*: lines between data points only serve for visualisation; they do not compulsorily reflect the real progress.

built up decelerated only marginally between 72 and 240 h of the experiment resulting in an end concentration of ~470 ppm iron.

The visual evaluation of the steel substrate depicted in Fig. 8 demonstrated a slightly blue annealing colour developing during corrosion experiments with both oil samples from oil A (derived from bench test run with and without contamination). Besides that, the oil sample from the run with addition of acetic acid caused spots of corrosion especially visible towards the cutting edges. The genuine part from corrosion experiments with oil C from reference run without contamination exhibited a lightly greyish annealing colour and almost no corrosion signs whereas the genuine part from the respective run with contamination showed heavy spots of corrosion again especially towards the cutting edges.

Different results compared to the iron concentration can be found for the copper concentration during the corrosion experiments, where no significant differentiation in the behaviour of the two oil qualities can be found. In this case, the common quality oil A possessed elevated dependence on the addition of acetic acid proved by the lowest corrosion potential of all investigated oils for the reference run without contamination, where a continuous increase of copper in the oil up to ~50 ppm throughout the experiment duration was observed. On the other hand, the oil sample from the bench test run with addition of acetic acid provoked the highest corrosion with a copper concentration up to ~100 ppm in the first 72 h of the experiment staying at this elevated level until the end of the experiment after 240 h. On the contrary, advanced technology oil C shows almost no dependency on the addition of acetic acid in the first 144 h of the experiment with copper concentrations lying between oil A in the reference run without contamination and oil A in the run with addition of acetic acid. Exceptional behaviour shows oil C from the reference run without contamination between 144 and 240 h of the experiment. In this time period the concentration rises to an

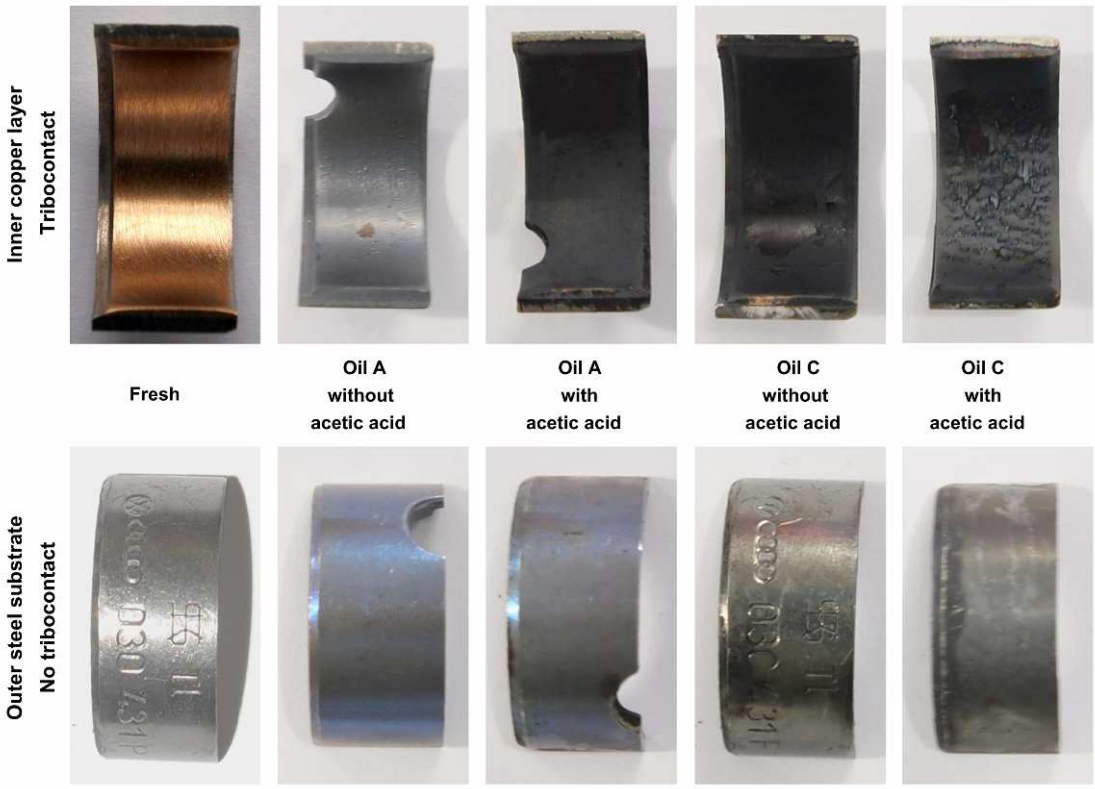

Fig. 8. Visual appearance of the small end bearings after 240 h of corrosion experiment.

unexpectedly high value of over 280 ppm copper. This value is confirmed by a second sampling. An explanation therefore is that after longer experiment duration flaking of the copper layer happened in the samples of oil C, only slightly in the case of the experiment with oil from the reference run but quite heavily during the corrosion experiment with oil from the run with addition of acetic acid. For this reason, the concentrations found are not reliable for the longest experiment duration (240 h) due to inhomogeneous distribution of metal in the oil. For example, a very low corrosion potential could be misleadingly concluded, if the flaking is not noticed. Therefore, a much higher corrosion attack during the experiment with the oil of the bench test run with acetic acid is assumed due to the most pronounced appearance of flaking.

It is, emphasised that the presented corrosion experiment was performed under static conditions with the consequence, that it does not consider rubbing of engine parts. It is concluded that the layer flaking off in the static experiment in the laboratory cannot be built up in the tribocontact due to continuous removal by the respective counter body in the bearing. For that reason, the laboratory experiment enables a more detailed study of inherent corrosion processes taking place while neglecting tribological influence. Provided that besides the determination of the elemental concentration in the oil also an accurate post-investigation of the respective specimen appearance with suitable surface analysis is carried out, two kinds of differentiation can be done: (1) differentiation between corrosion products that are dissolved and those forming reaction layers (as in this study) (2) differentiation between material loss preferably caused by corrosion or mechanical wear.

Fig. 9 displays SEM images of the inner surface of the small end bearing. Brittle deposits, partly peeled off, were found in all samples, supporting the conclusions from laboratory analysis (Figs. 7 and 8). The elemental composition of the deposits determined by EDX turned out to be similar with all oil samples with copper (18 to 63 at%) and carbon (18 to 74 at%) as main components as well as oxygen (3 to 12 at%) and surprisingly high concentrations of sulphur (4 to 17 at%). Tin (up to 5 at%) was found in areas, where the deposit layer was broken off, determined in spot 2 and spot 4, but not in the deposit layer itself, see spot 1 and spot 3. Other oil-specific elements such as calcium and phosphorus were not detected. For comparison, the fresh surface of the bearing is composed of 92 at% copper, 5 at% tin and 3 at% lead according to EDX. Based on these findings, it can be stated that sulphur from the engine oil as well as copper are main parameters affecting the corrosion mechanism taking place. More specific surface analysis, such as X-ray photoelectron spectroscopy, could give a deeper insight in the chemical composition, leading to a more refined corrosion mechanism hypothesis.

SEM investigation of the outer surface of the small end bearing showed, that the steel substrate is covered with a very thin layer of tin. During the experiments this layer is corrosively attacked resulting in spots of blank steel, where pronounced corrosion processes can take place. By EDX, low concentrations of organic deposits consisting of carbon and oxygen were found. The sulphur concentration was again elevated, especially on samples in contact with oil C.

The results of corrosion experiments carried out with the big end bearing are depicted in Fig. 10, where the concentrations of iron and aluminium in the oil samples are displayed over the whole period of the experiment. It can be stated, that obviously the aluminium layer,

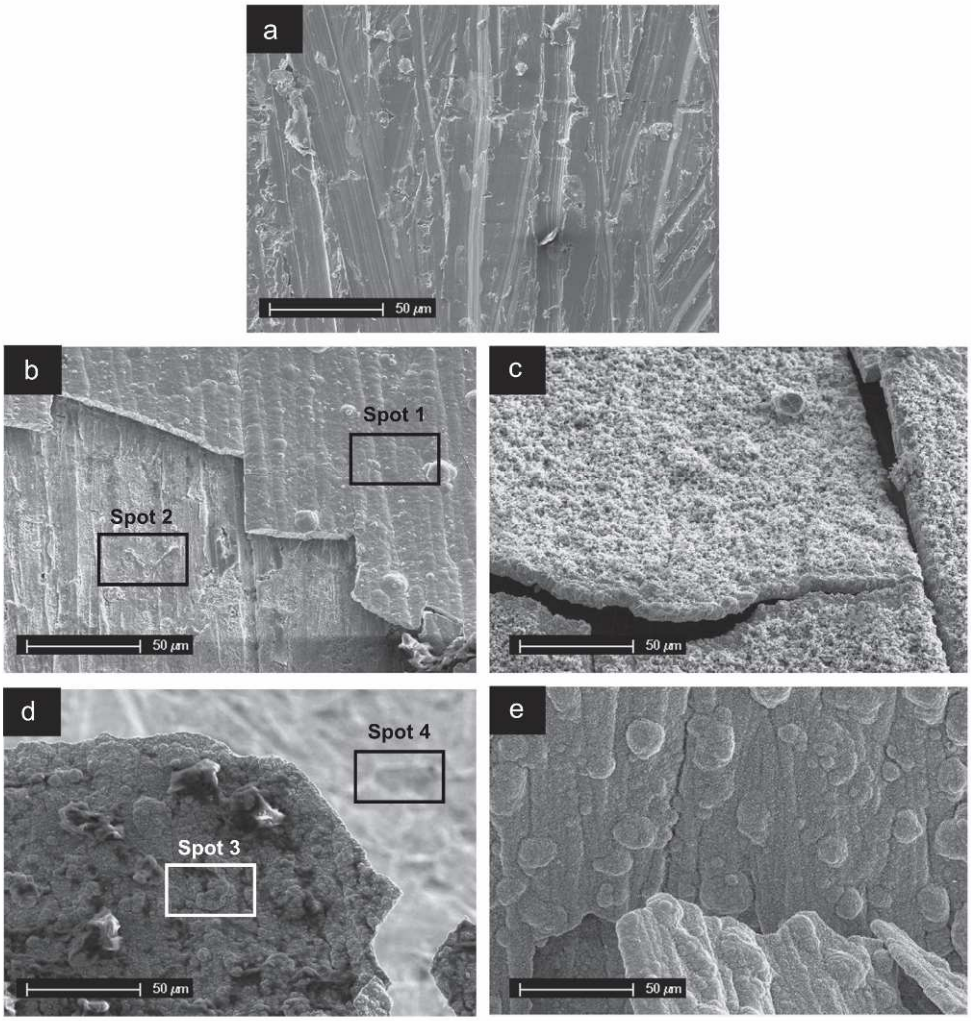

Fig. 9. SEM investigation of the small end bearing—inner surface: (a) fresh surface, (b) oil A without acetic acid, (c) oil A with acetic acid, (d) oil C without acetic acid, and (e) oil C with acetic acid.

where the tribo-contact happens, is not corrosively affected by any of the used oils expressed by levels of aluminium less than 5 ppm and an inconspicuous as well as unchanged appearance compared to the fresh parts, clearly shown in Fig. 11.

On the other hand, differences in the behaviour of the steel substrate are observed. Oils used in reference runs without contamination do not affect the steel substrate whereas oils from runs with acetic acid possess a higher corrosive impact on the steel substrate. This is proved by highly elevated levels of iron in the oil samples after the corrosion experiment similar to those found in the experiments with the small end bearing as well as by the formation of heavy black deposits on the outer steel surface during the 240 h of experiment. No significant difference can be seen between the two oil qualities during the first 144 h of experiment. Only in the end after 240 h oil C shows an increase up to ~450 ppm whereas oil A exhibits a plateau on about 370–380 ppm.

SEM investigations prove the findings made by laboratory data. It can be clearly stated, that the inner surface is not influenced by the corrosion experiment, indicated by a similar topography in comparison with the fresh bearing and by comparable element concentrations. The only marginal difference is sulphur, which can be found in traces after the corrosion experiment. Fig. 12 shows SEM images from the outer surface of the big end bearing. In this case, it is clearly shown that both oils from the reference runs without contamination do not have an influence on the bearing surface, neither on the topography nor on the elemental composition (Fig. 12) with 81 to 84 at% iron and 16 to 19 at% carbon. On the contrary, oil samples from runs with the addition of acetic acid provoke heavy deposit formation. The main elemental components in these deposits are carbon (27 to 45 at%) and oxygen (about 32 at%), followed by typical oil elements sulphur (up to 13 at%) and phosphorus, zinc and calcium to a low extent (up to 2 at%). The deposit layer seems to grow on the surface and appears to be brittle. In some places, the metal surface (75 at% iron) shines through (see Fig. 12 e) spot 1), again suggesting an alternating mechanism for deposit formation between build-up and decomposition, e.g. by flaking.

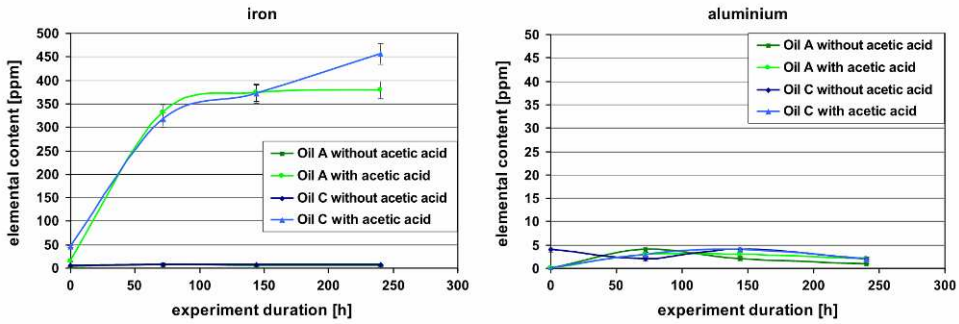

Fig. 10. Content of elements during laboratory corrosion experiment of the big end bearing. *Note*: lines between data points only serve for visualisation; they do not compulsorily reflect the real progress.

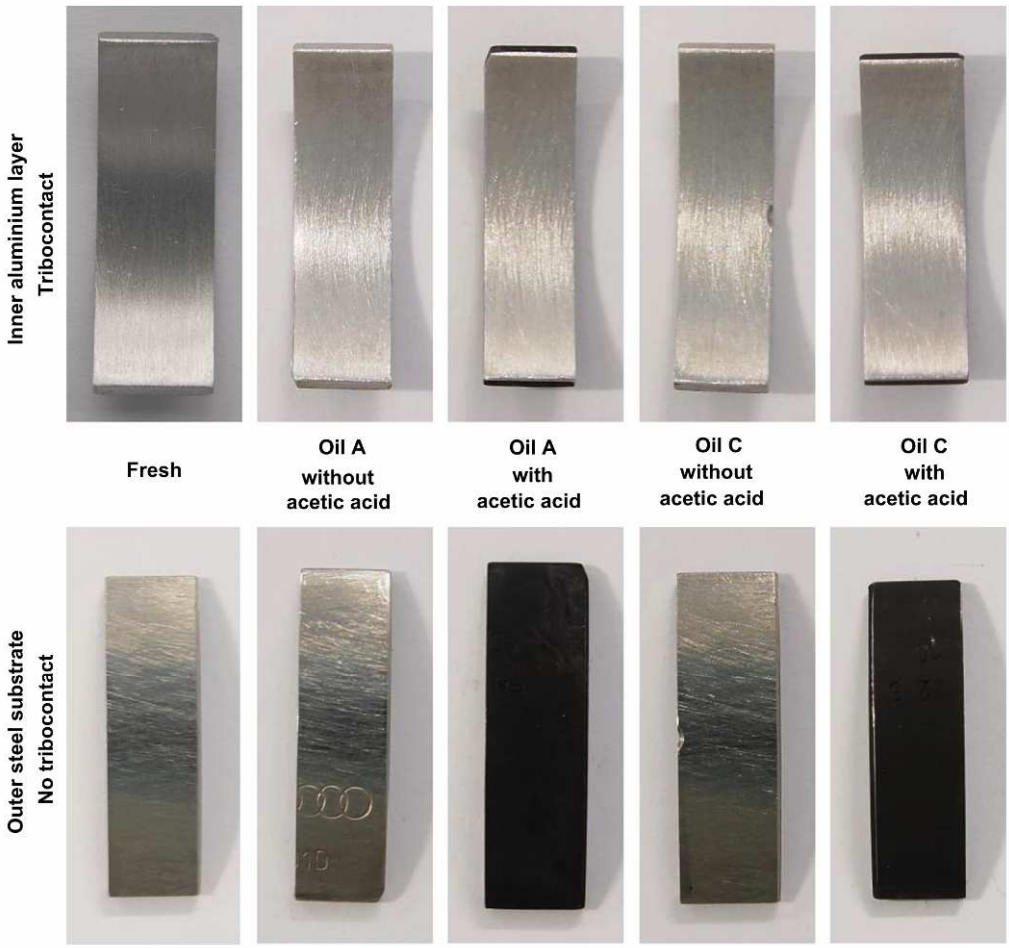

Fig. 11. Visual appearance of the big end bearings after 240 h of corrosion experiment.

3.4. Comparison of corrosion rates during static corrosion experiments in the laboratory and dynamic bench tests

Table 2 displays the parameters of the static corrosion experiments carried out in the laboratory and compares them to the conditions which predominated during the dynamic chassis dynamometer bench tests. It has to be emphasised, that both processes – corrosion and mechanical wear – can simultaneously take place during dynamic bench tests whereas in corrosion experiment solely the corrosive attack is taken into account. An acceleration of corrosion is expected

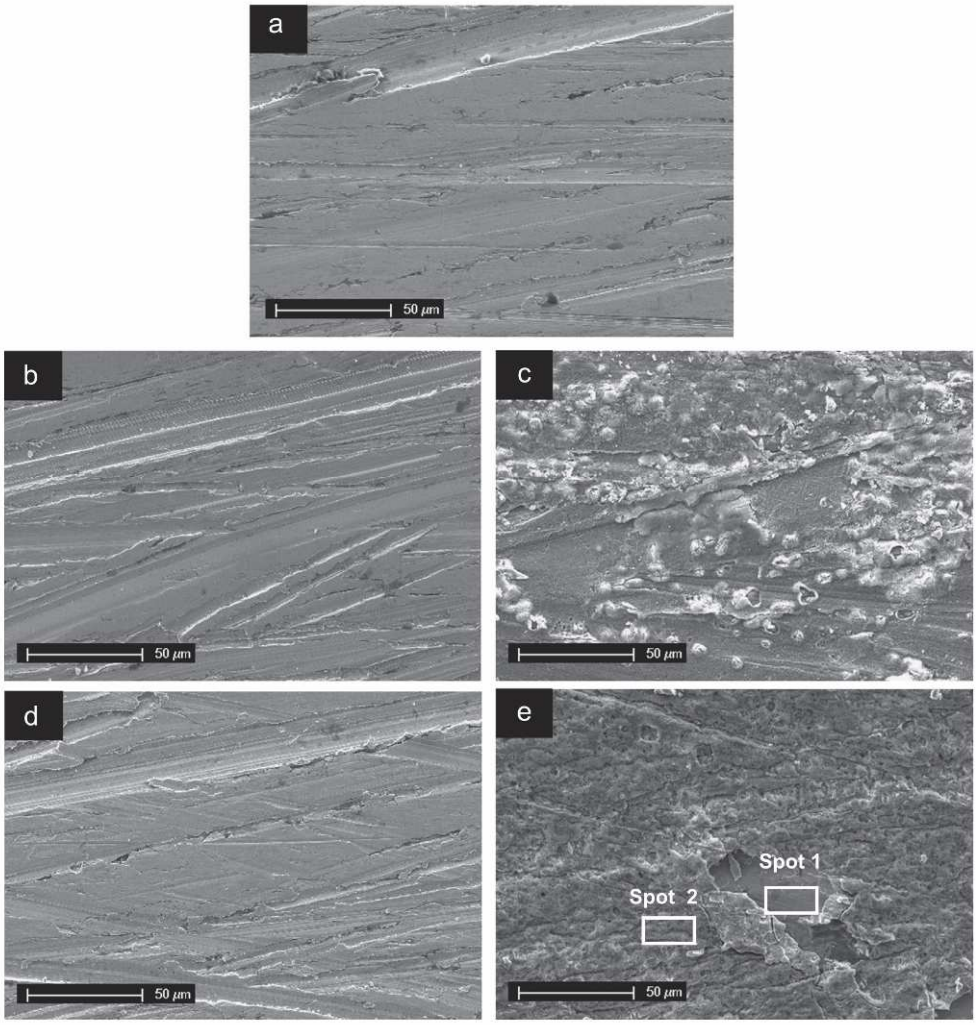

Fig. 12. SEM investigation of the big end bearing—outer steel surface: (a) fresh surface, (b) oil A without acetic acid, (c) oil A with acetic acid, (d) oil C without acetic acid, and (e) oil C with acetic acid.

Table 2
Comparison of experimental parameters of corrosion experiments in the laboratory and dynamic bench tests.

Experimental parameter	**Corrosion experiments in the** laboratory	**Dynamic bench tests**
Type of procedure	Static without movement of oil or engine parts	Dynamic oil flow as well as movement of engine parts
Type of stress to specimens	Corrosive attack	Corrosive attack and mechanical wear
Oil sump temperature	160 °C	Operation point 1: 110–115 °C Operation point 2: 125–130 °C
Duration	240 h	up to 80 h
Oil volume	8.5 mL	4500 mL
Engine parts exposed to stress	Bearings	Iron: all engine parts being in contact with oil Aluminium and copper: bearings
Ratio metal surface to oil volume	High (in the scale of 1 cm^2/mL)	Low (bearings: in the scale of 0.01 cm^2/mL)

due to an increased temperature in the laboratory corrosion experiments. Moreover, in the laboratory corrosion experiments, a prolonged duration and only a small oil volume were applied compared to the respective specimen surface immersed in the oil resulting in an easier detection of metals corroded by reason of concentration.

The mean corrosion rates during corrosion experiments in the laboratory as well as during the chassis dynamometer bench tests are summarised in Table 3. It is noted that in the dynamic bench tests "corrosion rate" stands for material loss caused by both corrosion and mechanical wear.

Without addition of acetic acid to oil A or oil C, the comparison of the mean corrosion rates of iron in both experiments suggests material loss was predominantly caused by wear. With the addition of acetic acid, the static corrosion experiments show a 2 to

Table 3
Mean corrosion rates per hour during experiments in the laboratory and during dynamic bench test.

	Mean corrosion rates per hour (ppm/h)						
	Corrosion experiments in the laboratory				Chassis dynamometer bench test		
	Iron[a]	Iron[b]	Copper	Aluminium	Iron	Copper	Aluminium
Oil A without contamination	0.0	0.0	0.2	0.0	0.1	0.0	0.0
Oil A with acetic acid	1.9	1.5	0.3	0.0	0.5	0.2	0.0
Oil C without contamination	0.0	0.0	1.2[c]	0.0	0.1	0.1	0.0
Oil C with acetic acid	1.3	1.7	0.3	0.0	0.8	0.2	0.0

[a] Small end bearing.
[b] Big end bearing.
[c] Unreliable value due to flaking.

4 times elevated mean corrosion rate of iron compared to the dynamic bench tests. Regarding aluminium, almost no aluminium was found in the oil samples collected from both types of procedure. For bearings with copper alloys, an enhanced sensitiveness towards corrosion in the presence of acetic acid can be stated in both corrosion experiments and dynamic bench test. However, oil A and especially oil C even without the addition of acetic acid exert some corrosiveness to copper-containing bearing materials.

Although oil A is characterised by a higher intrinsic acidification, i.e. higher initial NN than in oil C, iron and copper contents in the oil samples reveal a similar general trend of corrosiveness compared to oil C in all experiments (Figs. 2 and 7). In dynamic bench tests with addition of acetic acid, corrosion with oil C is more pronounced to iron which is attributed to higher levels of acetic acid available for interaction with the bearing surface. This is supported by the findings in Section 3.1.1. In static corrosion experiments, the individual results indicate that the impact of acetic acid could be attributed to different steel qualities applied (compare iron from small and big end bearing in Table 3). Copper is far less sensitive to such interactions, here oil A and oil C have a comparable performance after contact with acetic acid. The results clearly show that the differentiation of the oil performance needs to be carried out according to various aspects the individual weighting of which should result in the overall rating of performance.

The comparison of the corrosion rates in the static corrosion experiments and in the chassis dynamometer bench tests reveals, that both procedures generate corrosion rates in the same scale. Thus, the static laboratory experiments are basically possible to simulate the chassis dynamometer bench tests concerning the corrosion potential of various oil samples in the case of runs without the addition of acetic acid. In the case of addition of acetic acid, the increased corrosive impact in static experiments expressed by elevated corrosion rates proves the above-mentioned findings that wear – only observable in the dynamic bench tests – has only marginal impact on the formation of metal content in the oil.

4. Conclusions

The aim of the presented study was to investigate the influence of acetic acid, the partial combustion product of ethanol, on the engine oil performance by oil condition monitoring during chassis dynamometer bench tests. Additional failure assessments were made with machine parts disassembled from the passenger car operated at the bench test with special regard towards wear and corrosion. As third part, corrosion experiments were carried out in the laboratory in order to determine the corrosion potential of used oil samples from the bench test.

The results of the study prove that a good differentiation between bench test runs with and without addition of acetic acid can be found by evaluation of the conventional oil parameters, namely Total Base Number and Neutralisation Number. However, no conventional oil parameter reached critical values to recommend an oil change.

In contrast to these findings, metal contents indicated that these oils can possess corrosion potential. In the case of the present study, a corrosion potential towards iron and copper was found for oil samples from runs with the addition of acetic acid whereas in reference runs no built-up of these elements was observed in the oils.

Stoichiometric consideration of the addition of acetic acid showed that this acid is largely evaporated during engine operation, concluding that in common vehicle operation a rather low corrosion potential in the oil and consequently low risk of damage in the engine can be expected.

Failure assessment was carried out of used parts demounted from the passenger car after operation on the chassis dynamometer bench test. No signs of significant wear or severe corrosion were found on the investigated engine parts. Organic deposits were detected and identified on all machine parts investigated by SEM–EDX. The elemental composition of these layers was mainly carbon and oxygen together with the typical oil additive elements calcium, sulphur, phosphor, magnesium and zinc in low concentrations.

The observations of the corrosion potential of the oils sampled during the runs were corroborated by corrosion experiments carried out in the laboratory. Thereby, it could be shown that both oil samples A and C from the reference runs do not possess significant corrosion potential towards iron but elevated corrosion of copper. Both oil samples A and C from runs with addition of acetic acid proved to possess elevated corrosion potential towards iron as well as copper materials. Aluminium was not corrosively affected. These results underline the good correlation between results from the bench tests and results generated by laboratory experiments.

As long as the static corrosion experiments in the laboratory showed similar results than the supplementary analyses of oil samples from the dynamic bench tests, it can be stated that the main processes occurring in the engine can be connected with corrosion processes. Mechanical wear due to movements in the engine has only marginal influence as the surfaces were not significantly affected by wear scars. This hypothesis is supported by the evaluation of the mean corrosion rates of both types of procedure, showing a 2 to 4 times accelerated corrosion for static corrosion experiments with oils exposed to acetic acid. So, it could be demonstrated that the combined application of static laboratory experiments and dynamic bench tests allow a qualitative weighting between corrosion and mechanical wear as the dominating processes of material loss.

Acknowledgements

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2.3. Comparison of engine oil degradation observed in laboratory alteration and in the engine by chemometric data evaluation

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Comparison of engine oil degradation observed in laboratory alteration and in the engine by chemometric data evaluation

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ABSTRACT

The influence of ethanol in gasoline and its partial combustion products on the engine oil performance was investigated by joint use of IR spectroscopic data and chemometrics. Oil samples obtained from artificial alteration in the laboratory and engine alteration in a chassis dynamometer were compared. Quantification of residual amounts of antioxidant and antiwear additive (ZDDP) in the oil samples by FTIR spectroscopy showed depletion of phenolic antioxidant during engine alteration but ZDDP degradation during artificial alteration. Different chemometrical models using principal component analysis (PCA) elucidated similarities and differences between both alteration types, proving the findings of FTIR spectroscopy. Additionally, laboratory-based artificial alteration was mainly driven by oxidative processes whereas engine alteration showed higher amounts of both oxidation and nitration products.

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1. Introduction

For various reasons [1,2], there has been paid more and more attention to bio-fuels – especially fatty acid methyl esters for diesel substitution and ethanol for gasoline substitution, respectively – with the consequence that their production increased dramatically in the last decades and is still rising. At the present day, the quantities produced correspond only to 1% of fuel requirements but is expected to reach 7% until 2030 [3].

Legislation related to energy and fuels was the driving force concerned with these strategic, economical and environmental issues resulting in the directive 2003/30/EC [4], commonly known as the "bio-fuels directive", released by the European Union in May 2003. In this non-binding directive the replacement of 2% of all fossil fuels used in the transportation sector is demanded until December 31, 2005 as well as a further increase in substitution to 5.75% until December 31, 2010. With the new directive 2009/28/EC (RED—renewable energy directive) [5] from 2009 compulsory targets were introduced to replace 10% of common fuels by bio-components until 2020.

Intense research has been carried out on the topic of bio-diesel and its impact on the engine performance, on the lubrication system, and on the emission profile [6]. On the contrary, the interactions of bio-ethanol and its combustion products with the engine oil are still widely unknown resulting in a demand for detailed investigation due to highly usage as fuel in passenger cars. In Brazil, for example, ethanol became the second most consumed liquid fuel after diesel in 2008. This development is mainly attributed to the growing sales of flexible fuel vehicles. This technology enables the usage of gasoline–ethanol mixtures (also called gasohol) of any percentage in the same engine simultaneously and without any operational reconstruction [7].

In a recent study, Besser et al. [6] developed a novel thermo-oxidative alteration method to evaluate the impact of ethanol and its partial combustion products acetaldehyde and acetic acid on the engine oil while not yet considering other processes occurring in an engine like nitration or the impact of metal surfaces. It was clearly shown that ethanol and acetaldehyde have only marginal effects on the oil performance in comparison with artificial alterations using only air, but acetic acid decreased the oil stability resulting in accelerated degradation as well as a higher tendency towards sludge formation. In this paper, it is reported on complementary chassis dynamometer bench tests that have been performed to transfer the alteration system from the laboratory to the engine regime. As long as modern engine oils provide good stability, long-term engine bench tests are needed, exceeding 25,000 km, to provide differentiation between performances of individual oil formulations. In order to achieve accelerated deterioration of the lubricant during special time-saving bench tests, artificial alteration taking place directly in the engine was proposed to provide a significant shortening of test duration.

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Usually, a well-founded evaluation and in-depth understanding of oil deterioration mechanisms are based on the generation of extensive oil data by time and resources consuming methods, preferably by engine bench tests. This fact suggests the need to find different procedures being appropriate for a rapid and easy evaluation of the stability performance of novel oil formulations, in particular when a large number of oil samples has to be considered during such assessments. For this purpose, chemometrics is regarded to be thoroughly helpful as these statistical methods proved to provide substantial support in different fields of chemistry: Purcell et al. developed a rapid at-field screening method for sugarcane clonal performance using NIR spectra of the surface of sugarcane clones and chemometrics instead of a laboratory GC instrumental approach [8]. Friedl et al. presented a chemometric model to predict the higher heating value, the enthalpy of complete combustion of a fuel including the condensation of formed water, from the elemental composition of different biomass [9]. In lubricant chemistry, Gracia et al. combined mid-infrared (IR) spectroscopy with chemometrics to study oxidation processes occurring in lubricating base oils with and without the influence of iron by the means of principal component analysis. They showed that the first principal component is similar for oxidation with and without iron, but the second principal component reveals that iron provokes the formation of alcohols and esters, especially in the very first moments of the oxidation [10]. Gracia et al. presented in another publication investigations about the role of diphenylamine as an antioxidant in lubricating oils by combination of mid-IR spectroscopy with curve resolution methods [11]. Lima et al. investigated the carcinogenic potential of base oils as function of its concentration of polycyclic aromatic hydrocarbon compounds determined by near-IR spectroscopy utilising the tools of principal component analysis and principal component regression [12]. Sepcic et al. identified fresh and used engine oils based on the content of volatile compounds over the oils collected via headspace technique using solid phase microextraction and analysed by a time of flight mass spectrometer. Principal component analysis and cluster analysis were carried out to correlate these compounds with miles used in the engine [13]. Felkel et al. used chemometric tools to determine the total acid number of various gas engine oils from different gas engines using IR spectroscopic data [14]. By principal component analysis they proved that IR spectroscopic data reflect alteration mechanisms: qualitative differences between two engines types as well as between different oil fillings could be detected. They developed a partial least-squares model to predict the total acid number of used gas engine oils from IR spectroscopic data with a repeatability in the same range or better than potentiometric titration according to ASTM D 664 [15].

In this follow-up research work, statistical mathematical tools of chemometrics have been selected on the one hand to differentiate the stability performance of the engine oils and on the other hand to evaluate the correlation between artificial alteration in the laboratory and the natural as well as artificially accelerated alteration in the engine system. Chemometrics, especially principal component analysis (PCA), was selected as method of choice in this research work to evaluate the usefulness of statistical mathematical techniques for the investigation of engine oil degradation. In detail, PCA has been applied for the qualitative evaluation of differences or similarities in lubrication properties using variables derived from IR spectroscopic data. To our best knowledge, this is the first description reporting on the joint use of IR spectroscopic data and chemometrical tools for the interpretation of natural and artificial degradation of lubricating oils.

2. Experimental

2.1. Oil samples

In this study, oil samples from artificial alteration in the laboratory, from natural alteration in the engine regime as well as from artificially accelerated alteration in the engine regime were investigated. The procedures of sample generation are described in Sections 2.2.1 and 2.2.2.

Two fully formulated engine oils for the usage in passenger cars were chosen from a consecutive sequence of advancing engine oil technologies. Oil A with the viscosity grade SAE 15W-40 and the ACEA specification A3/B4 contains group I mineral base oil. It was selected to represent a common engine oil technology currently available on the market. Based on the performance of this oil during artificial alteration, improved formulations were developed, resulting in – among others – oil C with the viscosity grade SAE 5W-30 and exceeding ACEA specification A3/B4/C3. The main physical–chemical properties of oils A and C are given in Table 1 and discussed in detail in [6].

The elemental content was determined by optical emission spectroscopy with inductively coupled plasma of the aqueous solutions of the oils derived from microwave digestion with nitric acid. IR spectroscopic analysis showed the presence of aminic antioxidants in both oils, whereas phenolic antioxidants were found only in oil C.

2.2. Oil alteration

2.2.1. Artificial alteration in the laboratory

For the investigation of the influence of ethanol and its partial combustion products on engine oil, the above-mentioned fully formulated engine oils were altered with a novel artificial alteration method described in detail in [6]. The conditions for artificial alteration are summarised as follows: 300 g of the respective lubricating oil was placed in a round bottomed three-neck glass flask kept at 160 °C by a heating oil bath. The oil was brought into contact with dried air via a glass tube. The air gas flow was adjusted to 10 l/h by a flow controller. The flask was also equipped with a cooler to avoid considerable loss due to oil evaporation. One neck of the flask was used for periodical sampling and subsequent condition monitoring. The alteration duration was always 96 h, sampling was carried out every 24 h.

Three different liquid contaminations were added over the whole alteration period in order to simulate the influence of biofuels and its anticipated partial combustion products brought into the lubricant via blow-by gases and by down-washing from the cylinder liner wall. In detail, these compounds were ethanol and – as partial oxidation products and combustion by-products of ethanol – acetaldehyde as well as acetic acid. These combustion products were selected on the base of a literature research, where scientific work was found proving a correlation between the

Table 1
Physical—chemical properties of engine oil A and C [6].

Oil parameter	Oil A	Oil C
SAE grade	15W-40	5W-30
Total base number (mg KOH/kg)	8.1	7.2
Neutralisation number (mg KOH/kg)	2.0	1.4
Ca content (mg/kg)	2300	1900
P content (mg/kg)	700	700
S content (mg/kg)	4900	2100
Zn content (mg/kg)	900	800
Antioxidants	Aminic	Aminic, phenolic

usage of ethanol as bio-fuel blend and the formation of products like acetaldehyde and acetic acid (ethanoic acid) [16–18].

The addition of ethanol and acetic acid was provided by a dosing device via a Teflon tube in small portions to the bottom of the glass flask through the cooler. Due to the low boiling point of acetaldehyde (20 °C) and therefore its high volatility, the dosing device had to be cooled down ensuring the correct amount of substance being added. Additionally, a special sequence for dosing was developed to minimise the danger of explosion because of self-ignition of acetaldehyde.

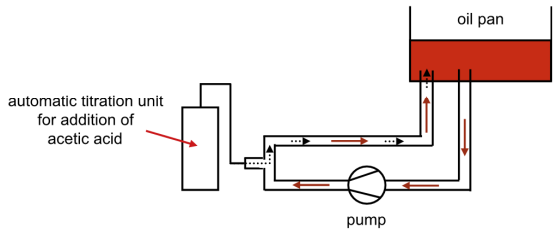

Fig. 1. Schematic setup for alteration acceleration in the real engine.

2.2.2. Alteration in the engine

In order to investigate the influence of ethanol and its partial combustion products on engine oil degradation in the engine regime and to correlate laboratory alteration with natural alteration, engine bench tests were carried out [19]. For the simulation of specific driving situations under reproducible conditions, a chassis dynamometer test bench was chosen. Experimental investigation was performed in a conventional passenger car equipped with a modern gasoline direct injection engine equipped with supercharging, which represented one of the latest generation of a downsizing concept to obtain higher engine loads. It had 1390 cm^3 displacement and 125 kW output at 6000 min^{-1}. The vehicle was run with conventional super unleaded gasoline of 2010 with a Research Octane Number of 95 and a total content of ethanol in the bio-components of 4.7% as prescribed by EN 228 of November 2008, where a maximum ethanol content of 5 vol% is defined [20].

A specially designed driving cycle was run consisting of two different steady state operation points applied in alternating manner: the first one with low road velocity, low rotational speed, and low load (operation point 1) and the second one with increased operating parameters (operation point 2). One driving cycle consisted of 30 min operation point 1 followed by operation point 2 for 1 h, closing with operation point 1 for 1 h. This driving cycle was performed twice a day covering the total distance of about 312 km per day. The oil temperature rose during the first 15 min of operation point 1 to 110–115 °C, further increased to 125–130 °C during operation point 2 and cooled down to 110–115 °C in the closing session applying operation point 1 again.

Sampling was done periodically in the end of each day directly after the second driving cycle through the oil dipstick tube. For further evaluation, the samples after four driving days were used, depicting 20 h, 40 h, 60 h, and 80 h of operating time .

Besides operation under conventional conditions, oil alteration in the real engine system was accelerated by artificial means in order to perform the engine tests within a reasonable time frame and to find out what correlations with artificial alterations in the laboratory could be achieved. According to the laboratory procedure described in Section 2.2.1, acetic acid – representing the contamination with the highest impact on oil degradation – was added continuously via a bypass system to the oil during engine operation (see scheme Fig. 1). Thereby, the oil was brought out of the oil pan (brown arrows) in a pump cycle and conducted via tubes to the inlet of an automatic titration device. There, acetic acid was dosed in small portions into the oil (dotted arrows), similar to the artificial alteration in the laboratory. Afterwards, the oil together with acetic acid was pumped back in the oil pan of the car.

Analogously to artificial alteration in the laboratory, engine-based alterations with acetic acid were compared to reference engine runs without addition of contamination.

For the engine bench tests, oil A which showed lower performance considering artificial alteration in the laboratory and oil C which turned out to be the best performer from artificial alteration were utilised. These engine oils were selected for time and cost reducing reasons and to screen the performance range of different oil formulations currently available in the market marked by oil A (lower performance) and oil C (high performance).

2.3. Oil condition monitoring

The results of the conventional oil parameters oxidation, total base number (TBN) and neutralisation number (NN) were already discussed in [6]. The oxidation value was determined by Fourier transform infrared spectroscopy (FTIR) using standard DIN 51453 [21], where the oxidation is given in absorbance per cm. It is calculated at the wavelength of 1710 cm^{-1} using the formula: oxidation (A/cm)= extinction (A)/thickness of cuvette (cm). The total base number (TBN) was measured using standard DIN ISO 3771 [22] by potentiometric perchloric titration. It stands for the amount of perchloric acid in equivalent mg of potassium hydroxide, which is required to neutralise all basic components in 1 g of oil sample. Neutralization number (NN) was determined using standard DIN 51558 [23]. NN depicts the amount of base needed to neutralise all acid components in 1 g of oil sample.

To provide further insight in oil deterioration, an in-depth investigation was carried out, especially concerning the depletion of additives during alteration in the laboratory as well as in the real engine. Thus, the residual amounts of both antioxidants – aminic and phenolic – and zinc dialkyldithiophosphate (ZDDP) as antiwear additive were determined based on IR spectroscopic data.

A time and cost consuming method for these investigations on the molecular level would have been gas chromatography coupled with mass spectrometry, exemplarily [24]. Instead, a more economic approach was to use FTIR spectroscopy for the determination of the residual concentration of several additives in the oil. Therefore, the relative concentrations of antioxidant and antiwear additive were determined by analysing characteristic absorption bands in the IR spectra of the individual oil samples measured with a Tensor 27 FTIR system (Bruker Optics, Ettlingen, Germany) using a 0.1 mm ZnSe cell. The scanning range was from 400 to 4000 cm^{-1} resulting in over 1800 data points. The peak area between 1530 and 1507 cm^{-1} was integrated with the software OPUS Version 5.0 (Bruker Optics, Ettlingen, Germany) [25] for the evaluation of residual aminic antioxidant content. For the determination of the content of phenolic antioxidants and antiwear additives, the absorbances (peak height) at 3651 cm^{-1} for phenols and 973 cm^{-1} for ZDDP were measured from the base oil corrected spectra using a virtual base line between absorbances at 1970 and 3800 cm^{-1}. The value for the fresh oil was taken as 100% and the respective residual value for the altered sample was determined as percentage thereof.

2.4. Chemometric evaluation

2.4.1. General introduction into chemometrics

Chemometrics, a discipline linking measurement-orientated chemistry and applied statistics, deals with the extraction of

information from chemical data by mathematical and statistical means and is part of chemoinformatics. As depicted in Fig. 2, multivariate data usually refer to n objects with m variables (features) building a matrix $\boldsymbol{X}$. The $n \times m$ matrix $\boldsymbol{X}$ contains a row for each of the n objects and a column for each of the m features. Objects can be any real or abstract items, e.g. oil samples as in this work, characterised by a set of variables (vector x_i^T). Variables are any numerical data, measured or computed, such as concentrations, absorption values, spectral peak heights or molecular descriptors. Spectroscopic data such as from FTIR are common variables in chemometrics and have been chosen for the development of chemometric models in this study. Properties represent interesting but difficult or not directly measureable data of the objects, e.g. origin of sample, biological activity of a compound, or presence of a substructure in a molecule [26].

There are three different approaches in chemometrics [26]:

1. The basic approach is exploratory data analysis (cluster analysis), where an evaluation of the similarity of the objects or the variables is done. The mostly used method is principal component analysis (PCA).
2. In another approach unknown objects are classified to one of two or more groups according to the similarity of their variables. Various multivariate classification methods are available, e.g. k-nearest neighbour classification (KNN), linear discriminant analysis (LDA), and discriminant partial least-squares regression (D-PLS).
3. The third approach in chemometrics is multivariate calibration. Thereby, mathematical models are developed to predict a property y from appropriate variables. Common methods of multiple regression are partial least-squares regression (PLS), principal component regression (PCR), and ordinary least-squares regression (OLS).

2.4.2. Concept of PCA

PCA is the most commonly used method to identify a trend or different clustering in multivariate data by significantly reducing the dimensionality in a multivariate data set. Thereby, latent variables as formal linear combinations of original variables are calculated to depict the Euclidean distances (as an inverse measure of similarity) between objects in the multivariate variable space. The direction preserving the relative distances best is the latent variable with maximum variance, called first principal component (PC1). The second principal component (PC2) is orthogonal to PC1 and provides the second largest variance after PC1. Further principal components are calculated according to the same procedure.

A linear latent variable is defined as follows:

$$u = b_1x_1 + b_2x_2 + \cdots + b_mx_m$$

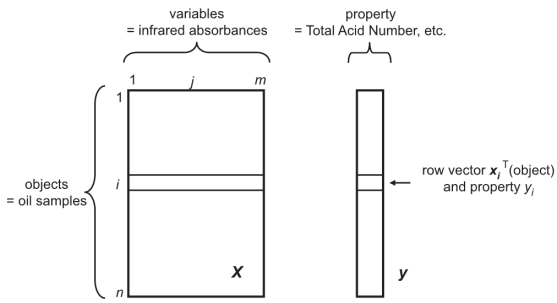

Fig. 2. Schematic illustration of multivariate data used in this work.

where u is the value of the latent variable also called score, x_i is the value of a variable, b_i is the loading, standing for the significance of the respective variable on the model, and m is the number of variables i.

A different mathematical description utilising vector notation

$$u = \mathbf{x}^T \cdot \mathbf{b}$$

where $\boldsymbol{x}^T$ is the object vector and $\boldsymbol{b}$ is the loading vector describing one direction in the m-dimensional space. The loading vector is usually scaled to the length of 1

$$b_1^2 + b_2^2 + \cdots + b_m^2 = 1$$

Scores and loadings can be used for illustrative score plots and loading plots, respectively, where different PCs can be plotted against each other [26].

PCA was carried out with the software The Unscrambler® version 9 [27].

3. Results and discussion

3.1. Data and object selection

For these investigations, oil samples from engine oil alteration both in the laboratory and the engine as well as the respective fresh oils were used as objects. Table 2 shows an overview of all alterations and the respective number of oil samples used for chemometric evaluations. There are three categories of oil samples: fresh oils and two different groups of altered oils, either in the laboratory or in the engine. From artificial alteration, four oil samples of each alteration type, reference alteration without contamination (only air) and alterations with the addition of ethanol, acetic acid or acetaldehyde, were taken into consideration. From engine-based alteration, five samples of reference alteration as well as of alteration with addition of acetic acid were taken from oil A, and eight samples of reference alteration and four samples of alteration with the addition of acetic acid of oil C were considered. The overall data set consisted of 56 samples as shown in Table 2.

In the first step, an overall model was built involving the whole data set described in Table 2. For further chemometric investigation, individual models with smaller data sets abstracted thereof were calculated separately.

3.2. Data preprocessing

As variables, IR spectroscopic data from background corrected absorption spectra were utilised. The total number of 1814 variables was reduced to 949 variables by spectroscopic based variable selection. Fig. 3 shows the selected areas over the total range of the spectrum each enframed in red. In detail, these are the areas with wave numbers from 3700 to 3100 cm^{-1}, from 1980 to 1480 cm^{-1}, and from 1370 to 640 cm^{-1}. Thereby, areas with obviously poor information content or total absorption as well as

Table 2
Overview of alterations and samples numbers selected for chemometrical evaluation.

Alteration type	Fresh oils		Artificial alteration		Engine alteration	
	Oil A	Oil C	Oil A	Oil C	Oil A	Oil C
Fresh oils	1	1	–	–	–	–
Reference	–	–	4	4	5	8
Ethanol	–	–	4	4	0	0
Acetic acid	–	–	4	4	5	4
Acetaldehyde	–	–	4	4	0	0

C–H and C–C bands were removed. For PCA all data sets have been mean centred.

3.3. Degradation of antioxidants and antiwear additives over time

3.3.1. Artificial alteration in the laboratory

Fig. 4 displays the degradation of the antioxidants, aminic in oil A and aminic as well as phenolic in oil C, during artificial alteration. It can be seen that there is practically no difference between the alteration types concerning phenolic antioxidants, whereas aminic antioxidants seem to be consumed much faster during alteration in the presence of acetic acid. The addition of acetaldehyde causes only slight depletion of aminic antioxidant. With ethanol, the same performance is observed as during the reference alteration which used only air. Thus, the addition of ethanol has no significant influence on antioxidant depletion.

An additional fact shown by these calculations is that the total amount of antioxidants never falls below 60% of the initial amount of the fresh oil, which hypothesises that the life cycle end of the oils has not been reached yet and the oils should be still considered appropriate for use.

Fig. 5 shows the residual amounts of antiwear additives (ZDDP) in the oils during artificial alteration in the laboratory. It can be seen, that ethanol as well as acetaldehyde have only marginal influence on the additive degradation confirmed by comparison with the reference alteration without addition of contamination. Contrarily, acetic acid provokes a significantly accelerated degradation of antiwear additives. It can also be stated, that a rapid decrease in additive content happens during the first 2 days of alteration, which is slowed down during the next 2 days. Eventually, it stabilises on a level of 20–30% in oils A and C. In this phase of alteration, the residual amount of ZDDP

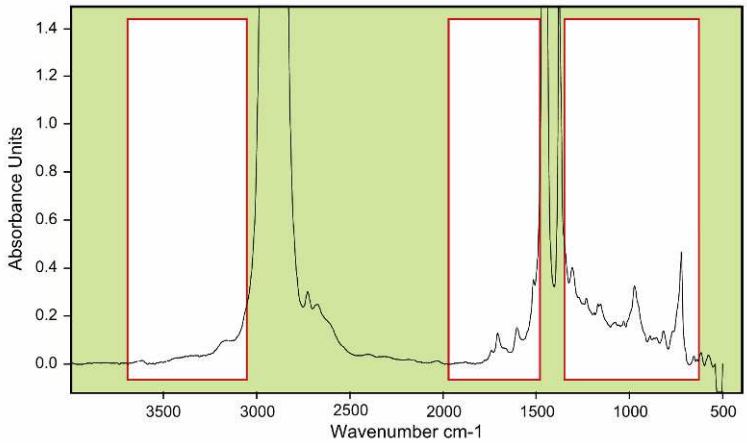

Fig. 3. Selected areas in the FTIR spectrum, areas in red frames signify FTIR data selected for PCA. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

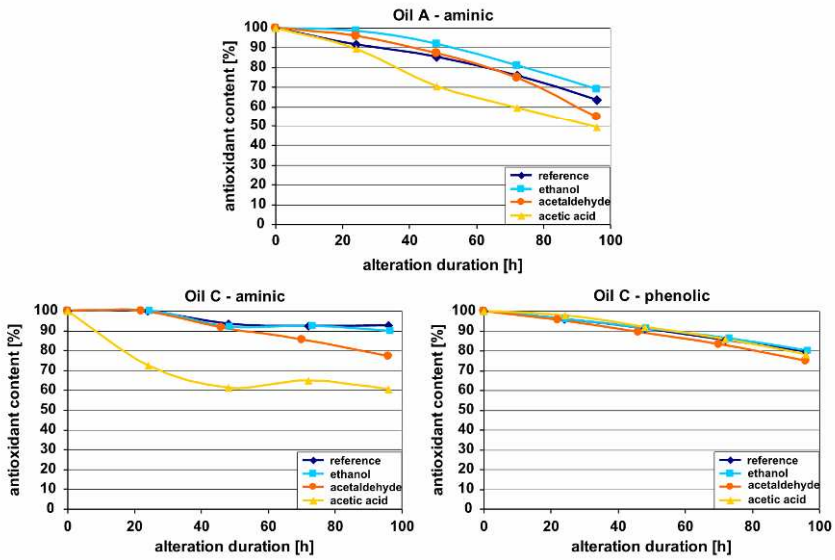

Fig. 4. Residual amount of antioxidants in oil A and C during artificial alteration determined by FTIR. Lines between data points only serve for visualisation, they do not compulsorily reflect the real degradation progress.

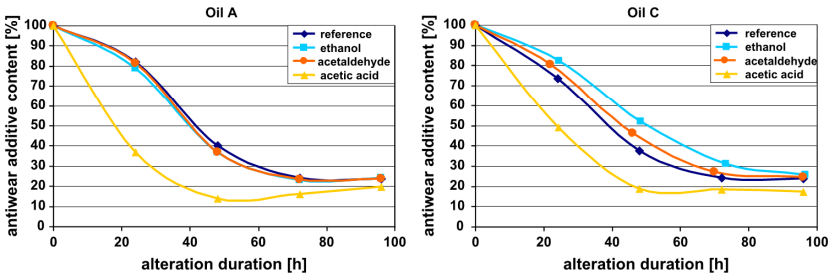

Fig. 5. Residual amount of antiwear additives in the oils during artificial alteration determined by FTIR. Lines between data points only serve for visualisation, they do not compulsorily reflect the real degradation progress.

seems to increase especially during alteration with the addition of acetic acid. However, it can be assumed, that this fluctuation is caused by measuring inaccuracy of up to 5%.

3.3.2. Alteration in an engine regime

Fig. 6 depicts the residual amounts of phenolic antioxidants and antiwear additives in the oils during engine alteration. For phenolic antioxidants, a much more rapid degradation in the engine could be observed in comparison with artificial alteration. It can be stated, that the degradation of antiwear additives in the engine is slower than that found during artificial alteration but it is also accelerated by the addition of acetic acid. The determination of the residual content of aminic antioxidants was not possible because of overlay of their significant bands by other degradation products. The findings suggest additional stress factors influencing the degradation processes in the engine, e.g. nitration (see end of Section 3.4.2).

3.4. Multivariate comparison of engine oil degradation

3.4.1. Overall PCA evaluation

For an overall PCA, all samples presented in Table 2 were chosen. So, the data matrix X consisted of 56 objects with 949 variables per oil sample. Figs. 7 and 8 depict the PCA score plot using the scores of the first two principal components PC1 and PC2 for all alterations selected. The sum of variances of PC1 and PC2 is only 63% for this model. Therefore, interpretation has to be done with caution regarding spectroscopic similarities of the oil samples depicted in the score plot.

Fig. 7 shows that samples from oils A and C are in separate regions (a full line defines the border). This separation indicates different oil chemistry of oils A and C on the one hand and different degradation behaviour on the other. PC1 (36% of total variance) represents the deterioration progress over time, which can be clearly confirmed in Figs. 7 and 8. For a better visualisation, the symbol size is proportional to the alteration duration. Fresh oils can be found on the left side of the score plot, while the amount of degradation develops with increasing alteration duration along the x-axis (PC1) towards the right side.

In contrast, PC2 (27% of total variance) stands mainly for the oil chemistry, which is deduced from the disposition of the clouds of the two oils regarding the y-axis of the score plot.

Another fact shown by Fig. 7 is the information about the different degradation behaviour of the two oils. Oil A forms a more diffuse and stretched cloud than oil C. This is an indication for the higher stability of oil C regarding stresses caused by artificial and engine alteration applied. Shorter distances between individual spots – or individual oil samples – mean larger similarity or in other words the differences between altered samples and fresh oil are smaller. This result confirms the findings made earlier using conventional laboratory data [6].

Fig. 8 shows the same PCA score plot of oil A and oil C as in Fig. 7 but provides other information. Here, the influence of the different contaminations added during alteration can be evaluated. The reference alterations as well as the alterations with the addition of ethanol and acetaldehyde, respectively, are depicted in equal symbols (circles). Samples from alterations with the addition of acetic acid are represented by squares. The results based on conventional oil parameters measured in the laboratory can be verified concluding that ethanol and acetaldehyde have almost no influence on engine oil deterioration. This can be seen very clearly especially in the cloud of oil C. There the sample scores from alterations with ethanol and acetaldehyde are almost at the same place as scores from reference alteration with air. In the cloud of oil A, the phenomenon is less pronounced than with oil C. This results from a lower stability of common technology oil A in view of the strains of alteration applied, also found in laboratory data. Obviously, it can be stated that acetic acid is the only contamination with a significant influence on the degradation process.

Besides the consideration of the clustering and placement of the two oils in the score plot as well as the influence of various contaminations on the degradation progress, the comparison of artificial alteration samples from the laboratory with those obtained by engine bench tests is of great interest. The above-mentioned score plots (Figs. 7 and 8) demonstrate the origin of the different oil samples. The chemometrical findings confirm that for both oils the engine alteration fits only partially to artificial alteration concerning the location of the scores in the score plot in this special model. In order to investigate the reasons for this difference between laboratory and engine degradation mechanisms, more suitable chemometrical models for each oil were developed. The model for oil C is exemplarily shown in the following section.

3.4.2. Chemometrical comparison of artificial and engine alteration

For this investigation, a PCA model has been computed using all 22 samples from oil C, presented in Table 2. Fig. 9 depicts the PCA score plot using the principal components PC1 and PC2. The explained variance from PC1 is 51% and from PC2 is 37%, indicating a good representation of the relative distances in the high-dimensional space.

The differentiation of artificial alteration in a laboratory device and on a chassis dynamometer test bench is again demonstrated. An interesting fact is the similar appearance of both regimes. For example, artificial reference alteration and artificial alterations with the addition of ethanol and acetaldehyde behave similar to the reference alteration in the engine. Furthermore, both alterations with the addition of acetic acid, in the laboratory as well as

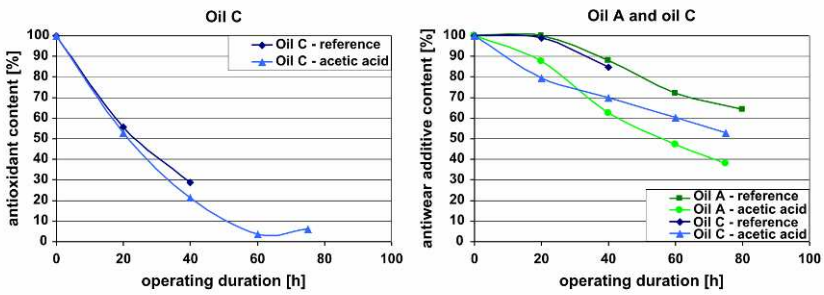

Fig. 6. Residual amounts of phenolic antioxidants and antiwear additives in oils A and C during engine alteration determined by IR spectroscopy. Lines between data points only serve for visualisation, they do not compulsorily reflect the real degradation progress.

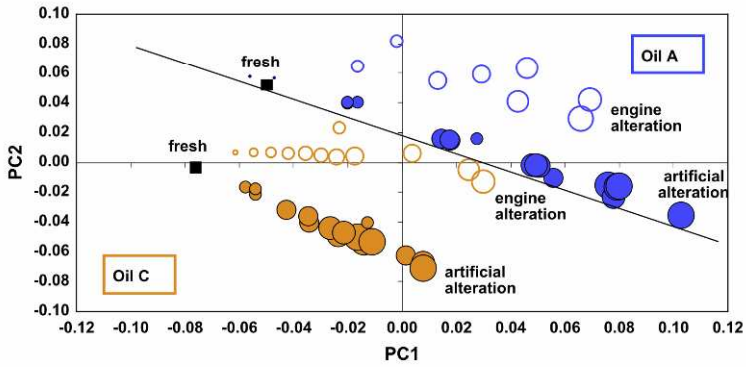

Fig. 7. PCA score plot of oils A and oil C—full line emphasises border between oils A and C. Size of symbols is proportional to alteration duration, black squares depict fresh oils, full symbols indicate alteration in the laboratory, and empty symbols indicate alteration in the engine.

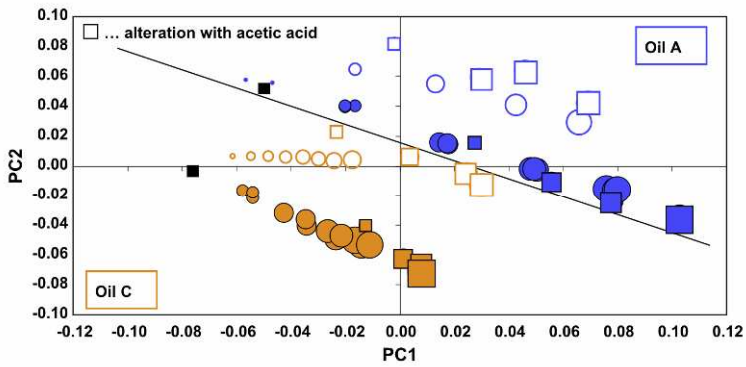

Fig. 8. PCA score plot of oils A and oil C. Size of symbols refers to alteration duration, black squares depict fresh oils, full line emphasises border between oils A and C; circles depict reference alterations, alterations with ethanol and alterations with acetaldehyde, squares depict alterations with acetic acid; full symbols indicate alteration in the laboratory, and empty symbols indicate alteration in the engine.

in the engine, show the same appearance far apart from the remaining alterations. That means that the same mechanisms in both regimes basically take place and bio-components from the fuel and its partial combustion products have the same impact on the degradation behaviour in both cases. The different locations of the clouds for artificial and engine alteration indicate additional parameters in the oil degradation besides contamination, e.g. different oil chemistry. These processes are investigated in the following part of this section.

The distance between the fresh oil and oil samples from alteration with acetic acid is larger for engine alteration than for artificial alteration.

A further interesting finding is the orientation of the different alteration types. The deterioration progress seems to go mainly

along with PC2 whereas the chemical influence of added contaminations is displayed in PC1 as it is clearly demonstrated in Fig. 9. This is a finding contrarly to the model containing both oils A and C and implements that, regarding only one oil, the greatest variance between the samples does not lie in the degradation process itself but in the different chemical conditions the addition of contaminations provokes. This applies especially to oil C and can be attributed to its high stability against oil degradation.

For further investigation of the reasons for the differences between alteration in the laboratory and in the engine, the PCA loading plots for oil C were used to gain deeper insight in the influence of the involved variables Fig. 10.

In the score plot (Fig. 9), a tendency can be seen for samples from longer alterations being located at the right hand side of the plot (thus having large values for the PC1 score). Because of the mathematical properties of PCA, the corresponding loading plot (Fig. 10) illustrates that the variables located at the right hand side have in general high values for these altered samples. Actually, the variables within the (manually drawn) red box are the absorbances at wave numbers from 1555 to 1615 cm^{-1}. This is the absorbance region especially of carboxylates, most likely formed from carboxylic acids during alteration with the addition of acetic acid due to degradation.

In order to confirm this hypothesis, a PCA model was recalculated excluding the variables in the red frame. The resulting score plot is shown in Fig. 11, and the respective loading plot in Fig. 12.

In the score plot, a "shift" of the acetic acid alterations towards the other alterations can be seen supporting the assumption proposed above. Nonetheless, it is pointed out, that additionally other factors besides the direct impact of acetic acid took place or were induced by the contamination. This is reflected by the fact, that even with the recalculation the alterations with acetic acid cannot be transferred exactly into the cloud of the remaining alterations.

After reducing the influence of acetic acid, two significant areas were built up in this chemometrical model each representing either alteration in the laboratory or in the real engine. The influencing factors can be found in the corresponding loading plot depicted in Fig. 12.

In the loading plot, two areas can be assigned rather to the artificial alteration in the lower part and rather to the engine alteration in the upper part, respectively. A closer look at the individual wave numbers being in the particular regions gives information about the major degradation influencing parameters in each regime. In this examination, special attention was paid to antioxidants and antiwear additives as their residual amounts obtained by conventional condition monitoring were item of in-depth investigation to gain knowledge about oil degradation mechanisms (see Section 3.3.1). The two wave number regions significant for these structures are marked by red boxes in Fig. 11. These are the region from 3645 to 3655 cm^{-1} in the area of artificial alteration for phenolic antioxidants and the region from 960 to 990 cm^{-1} in the area of engine alteration for ZDDP, respectively.

The location of the loadings and therefore the corresponding variables correlate with the scores found in the same section of the plot and implies that these variables have a strong influence on the scores.

Basically, strong bands in the spectra lead to high loading values and, as a consequence, have more impact on the location of the respective score. Thereby, it has to be differentiated, whether bands of the IR spectra are disappearing due to additive depletion or growing due to alteration product built-up during alteration. In the first case, especially antioxidants and antiwear additives have to be mentioned (wave numbers in red frame in Fig. 12). The significant absorption band of antioxidants (wave numbers 3645–3655 cm^{-1}) can be found in the region of artificial alteration. Therefore it can be stated, that during the whole artificial alteration a considerable band at the respective wave numbers can be found concluding, that antioxidants are hardly degraded during artificial alteration. Different behaviour can be found for antiwear additives the significant absorption bands (960–990 cm^{-1}) of which appear in the region of engine alteration resulting in the proposition that under these alteration conditions antiwear additive degradation is slower than in artificial alteration. These findings verify the results of additive degradation carried out by IR spectra evaluation and presented in Section 3.3.1, where a pronounced depletion of antiwear additives during artificial alteration in the laboratory and an increased degradation of phenolic antioxidants during alteration in the engine could be observed (Figs. 4–6). The reason for the accelerated degradation of antiwear additive lies most probably in the thermal stability of this compound. ZDDP decomposes at temperatures above 100 °C [28]. Artificial alteration was carried out at 160 °C whereas the oil temperature in the oil pan of the engine lay between 110 and 130 °C and only a small volume is exposed to elevated temperatures in the combustion chamber, supporting the findings discussed above that ZDDP depletion is accelerated during artificial

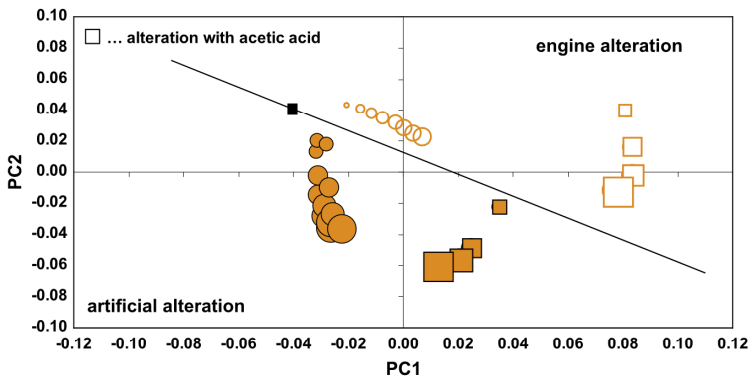

Fig. 9. PCA score plot of oil C. Size of symbols refers to alteration duration, black square depicts fresh oil, full line emphasises border between artificial alteration in the laboratory and alteration in the engine; circles depict reference alterations, alterations with ethanol and alterations with acetaldehyde, squares depict alterations with acetic acid; full symbols indicate alteration in the laboratory, and empty symbols indicate alteration in the engine.

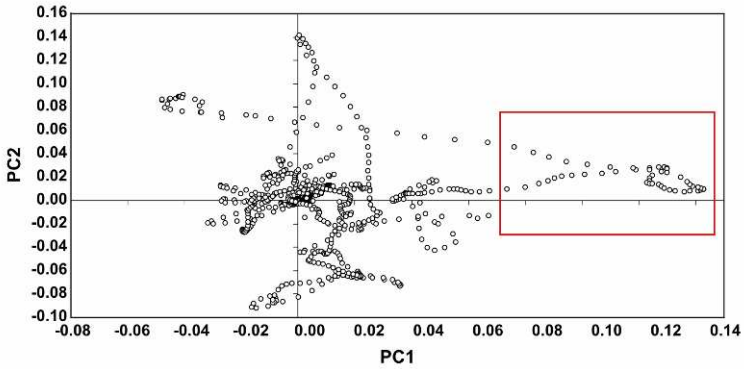

Fig. 10. PCA loading plot of oil C. Variables in red frame derive from acetic acid. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

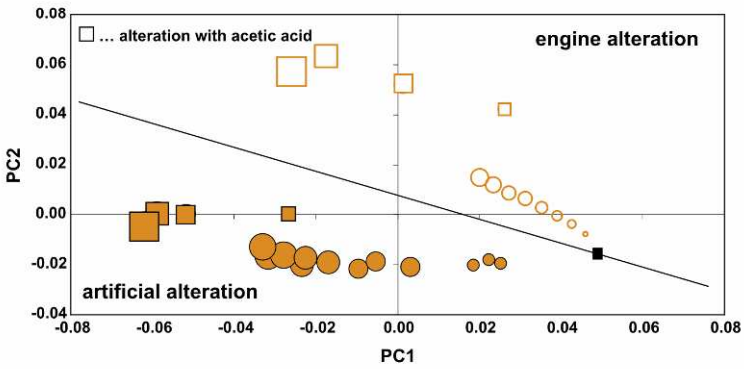

Fig. 11. PCA score plot of oil C obtained after exclusion of FTIR data relating to carboxylates. Size of symbols refers to alteration duration, black square depicts fresh oil, full line emphasises border between artificial alteration in the laboratory and alteration in the engine; circles depict reference alterations, alterations with ethanol and alterations with acetaldehyde, squares depict alterations with acetic acid; full symbols indicate alteration in the laboratory, and empty symbols indicate alteration in the engine. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

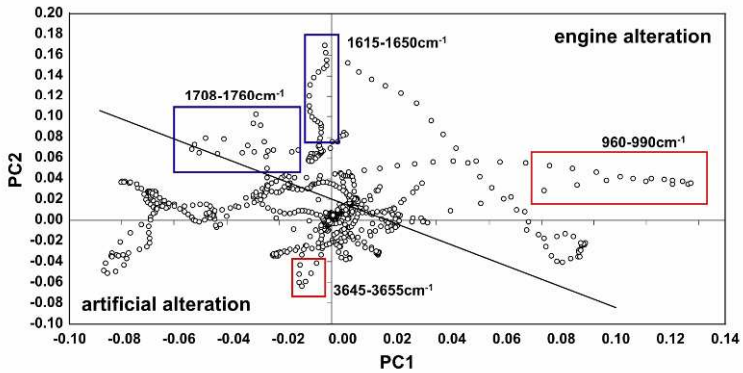

Fig. 12. PCA loading plot of oil C obtained after exclusion of FTIR data relating to carboxylates. Variables in the red boxes standing for additives—ZDDP (960–990 cm^{-1}) and phenolic antioxidants (3645–3655 cm^{-1}) respectively. Variables in the blue boxes standing for oil degradation products—oxidation (1708–1760 cm^{-1}) and nitration (1615–1650 cm^{-1}) respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

alteration compared to engine alteration. On the other hand, the more rapid depletion of antioxidants during engine alteration indicates that during engine alteration many higher oxidative processes probably linked with nitration processes take place besides thermo-oxidation considered in the laboratory set-up.

In the second case of alteration product built-up, mainly two wave number regions were found in the loading plot to have high influence (blue frame in Fig. 12): wave numbers between 1708 and 1760 cm^{-1} significant for oxidation and the region between 1615 and 1650 cm^{-1} significant for nitration, respectively [21].

Oxidation can be found in both regions, from artificial and engine alteration, implying that oxidative processes occurred in both alteration regimes. The significant bands for nitration show different results. Their loadings are located in the area of engine alteration. The reason thereof is that during engine operation various nitrous fumes are built which interact with the engine oil. It is expected that the consideration of nitrous fumes in the artificial alteration set-up would result in the shift of the respective loadings towards the area of engine alteration.

These findings can be used as valuable input for adapting the artificial alteration device to an even "closer-to-reality" device, which can simulate the processes in an engine more comprehensively. One possible approach could be the involvement of nitrous fumes and thereby inducing nitration processes during alteration.

Finally, it can be stated that loadings reflecting additive IR absorption bands appear rather on the right and lower side of the plot near the fresh oil scores whereas oxidation and nitration products can be located rather on the left side of the plot. This emphasises the direction of the degradation progress found in the score plot of this modified model (see Fig. 12).

4. Conclusions

These investigations covered the impact of bio-fuels on the engine oil stability. Thereby, two fully formulated engine oils were artificially altered in a novel laboratory alteration device as well as evaluated in a chassis dynamometer test bench.

In the course of an in-depth oil condition monitoring, the residual amounts of antioxidants as well as anti-wear additive (ZDDP) were determined. Thereby it was found, that especially aminic antioxidants are depleted faster during artificial alteration with the addition of acetic acid whereas the addition of ethanol and acetaldehyde showed no significant influence. Nonetheless, the total amount of antioxidants never fell below 60% of the initial amount in the fresh oil. Similar results were obtained with ZDDP in artificial alteration, proving that ethanol and acetaldehyde provoked similar ZDDP depletion compared to the reference alteration without addition of contamination, whereas acetic acid caused a more rapid decrease. Additionally, it was found that the amount of ZDDP during artificial alteration dropped down to a low level of 20–30%.

During alteration in the engine a pronounced degradation of phenolic antioxidants was observed compared to artificial alteration in the laboratory. On the contrary, the depletion of ZDDP in the engine was slower than that during artificial alteration but also showed acceleration by acetic acid.

For the differentiation of the degradation mechanisms of the engine oils during artificial alteration in the laboratory as well as during chassis dynamometer bench test, a novel interpretation tool based on IR spectroscopic data treatment using PCA was demonstrated. Chemometrical results proved that for both oils the engine alteration fits only partially to the artificial alteration in the laboratory mainly due to the reason, that nitration processes are important contributors to degradation mechanisms taking place in the car but are not yet considered in the laboratory set-up. Generally, it can be stated that the chemometrical findings emphasise and better visualise the results of additive degradation than those obtained by traditional IR spectra evaluation.

The chemometric approach proposed proved to be suitable for the investigation of engine oil degradation. It could be demonstrated that the generation of appropriate chemometric models and their modification allows a more systematic approach to an in-depth understanding of engine oil degradation in comparison with the findings based on conventional lubricant data.

The differences and knowledge of the reasons for such differences found between artificial alteration in the laboratory and alteration in the engine are helpful for the adaptation of artificial alteration parameters for a better correlation between alteration in the laboratory and in an engine. Consequently, valuable input is provided for future work comprising the development of novel artificial alteration methods with an even higher degree of comparability to real operating conditions where additional processes besides thermo-oxidation could be involved.

Acknowledgements

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3. Conclusions

The aim of the thesis was to investigate the impact of ethanol and its partial combustion products on the performance of engine oils designated for the application on vehicles fuelled with bio-ethanol blended gasoline.

In the first step, a novel set-up of artificial alteration was developed especially for the simulation of stress conditions predominating in bio-fuelled engines. This intent was realised by the addition of selected liquid contaminations, i.e. ethanol, acetaldehyde, and acetic acid to the oil sample throughout the thermo-oxidative artificial alteration of engine oil samples.
The potential of this lab-based method was demonstrated by the stepwise adaptation of engine oil formulations regarding their stability against strains prevailed in vehicles run with bio-ethanol containing fuels. By the introduction of this method, various benefits could be achieved, such as the possibility to compare reference alterations carried out thermo-oxidatively according to currently available standards to artificial alterations with the addition of application adapted contaminations resulting in a clear statement about the impact of the respective fuel component on the alteration characteristics of the engine oil.
The method enables a pre-selection of oil formulations according to their performance under the chosen conditions with the advantage being a short-term procedure for the investigation of the long-term oil behaviour. Consecutive condition monitoring allows a tracking of the oil degradation throughout the alteration duration. The method is highly flexible affording the opportunity to vary alteration parameters to requested engine conditions representing a time and cost efficient alternative prior to expensive engine bench tests. It offers the possibility to investigate contaminations independently from other influences hence eliminating interferences complicating data interpretation.
By means of this method, it was proved, that ethanol as well as acetaldehyde possesses only marginal influence on the alteration characteristics of the engine oil formulations in terms of conventional oil condition parameters. On the contrary, acetic acid was identified to advance oxidation processes and induce significant sludge formation.

As a consecutive step of the study, chassis dynamometer bench tests were carried out evaluating fully formulated engine oils, which were also applied in laboratory artificial alteration, under engine conditions, hence validating results gained in the lab. For these experiments, the two oils with the best and the worst performance, respectively, during artificial alteration in the lab were chosen. Furthermore, the attempt was made to transfer

artificial alteration acceleration from the laboratory to the engine system, on the one hand to perform the tests within a reasonable time frame and on the other hand to achieve additional correlations between the two conditions. According to the laboratory procedure, acetic acid, representing the contamination with the highest impact on oil degradation, was added continuously via a bypass system to the car's oil circuit.

Additional failure assessment was performed with machine parts dissembled from the passenger car operated at the chassis dynamometer bench test with special focus on wear and corrosion. Moreover, corrosion experiments were carried out in the laboratory to determine the corrosion potential of used oil samples from the bench test.

A good differentiation was found between bench test runs with and without the addition of acetic acid in terms of the conventional oil alteration parameters, such as Neutralisation Number and Total Base Number, even though no oil parameter reached critical values to recommend an oil change. However, the metal contents of these oils indicated an elevated corrosion potential – especially towards iron and copper – of oil samples from runs with acetic acid addition whereas in reference runs without contamination no built-up of metals in the oils was observed. Stoichiometric calculations of the acetic acid addition ensured a large evaporation of the acid during engine operation suggesting a rather low corrosion potential in common vehicle operation and, thus, a low risk of damage in the engine.

By failure assessment of demounted parts, no signs of significant corrosion or severe wear were detected. Organic deposits, found on all investigated parts, consisted mainly from carbon and oxygen together with typical oil additive elements such as calcium, sulfur, phosphor, magnesium, and zinc, in low concentrations.

Corrosion experiments carried out in the laboratory corroborated the observations of the corrosion potential of oils sampled during engine runs. It was shown, that oils from the reference runs without addition of contamination do not possess significant corrosion potential towards iron but provoked elevated corrosion of copper. Samples from runs with the addition of acetic acid exhibited elevated corrosion potential towards iron as well as copper materials. Aluminium was not affected by corrosion. These results emphasize the good correlation of results from static laboratory experiments with results gained from the dynamic bench test. Hence, this leads to the suggestion that the main processes occurring in an engine can be connected with corrosion processes, whereas mechanical wear due to engine part movement has only marginal influence since no significant wear scars were found on the metal surfaces. The mean corrosion rates of both procedure types support this hypothesis by showing a 2 to 4 times accelerated corrosion for the static laboratory experiments with oils

which were brought in contact to acetic acid. By theses means, a qualitative weighting between corrosion and mechanical wear as the dominating processes of material loss was achieved by the combined application of static laboratory experiments and dynamic bench tests.

The concluding part of the study comprised an in-depth oil condition monitoring with the focus on the determination of residual amounts of antioxidants as well as anti-wear additives zinc dithiophosphate (ZDDP) of oil samples collected during artificial alteration in the laboratory as well as during chassis dynamometer bench tests. It was observed that especially aminic antioxidants are degraded faster during alteration with addition of acetic acid whereas ethanol and acetaldehyde possessed no significant impact. Nonetheless, the decrease of the total amount of antioxidants was not greater than 40 % of the initial amount in the fresh oil. Similar results were achieved with ZDDP with almost no impact of ethanol and acetaldehyde but an accelerated decrease during the addition of acetic acid.
Moreover, it was found that the ZDDP concentration dropped down to the low level of 20 to 30 % during artificial alteration. A comparison of additive degradation in samples of laboratory alteration with samples from the engine showed a pronounced degradation of phenolic antioxidants during engine operation, whereas the depletion of ZDDP in the bench test was slower but also showed acceleration by the addition of acetic acid.

Furthermore, a novel interpretation tool based on IR spectroscopic data treatment was demonstrated using principal component analysis (PCA). In doing so, the aim was to find a differentiation of the engine oil degradation mechanisms during artificial alteration in the laboratory as well as during the bench test.
The results from this chemometric approach proved that both alteration systems fit only partially mainly due to the reason, that important contributors to degradation taking place in the car are nitration processes, which are not yet considered in the laboratory set-up. In general, it was proven that chemometrical findings emphasise and better visualise results of additive degradation compared to traditional IR spectra evaluation. The chemometric approach was found to be suitable for the evaluation of engine oil deterioration by the generation of appropriate chemometric models and their modification, hence allowing a more systematic access to an in-depth understanding in comparison with the findings based on conventional lubricant data.
The identification of the differences and reasons therefore between artificial alteration in the laboratory and alteration in the engine are a highly important input for a further adaption of

artificial alteration parameters for an even better simulation of the real conditions in a laboratory set-up.

Consequently, a valuable contribution is provided for future research work involving the development of novel artificial alteration methods with an even higher comparability to real-life operation conditions including additional processes besides thermo-oxidation.

4. Curriculum vitae

Personal data

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Education

Since 03/2009	PhD studies at Vienna University of Technology, Austria Faculty of Technical Chemistry, Institute of Chemical Technologies and Analytics
10/2000 – 08/2007	Master of Science (Mag. rer. nat.) at the University of Vienna, Austria Faculty of Chemistry, Institute of Analytical Chemistry

Professional experience

Since 09/2011	Project leader – Multifunctional concepts for Lubricants with synthetic components at the Austrian Excellence Center of Tribology, AC²T research GmbH, Wiener Neustadt, Austria
Since 02/2008	Scientist – Lubricants and surface interactions at the Austrian Excellence Center of Tribology AC²T research GmbH, Wiener Neustadt, Austria
09/2006 – 02/2007	Internship – Oil condition monitoring at the OMV GmbH, Vienna, Austria
03/2006 – 08/2006	Master thesis „*Untersuchung der thermo-oxidativen Stabilität von Industrieschmierölen*“ at the OMV GmbH, Vienna, Austria
10/2005 – 02/2006	Internship – Oil condition monitoring Large Engines Competence Center (LEC), Graz, Austria

Publications

Peer reviewed publications

Besser C., Steinschütz K., Dörr N., Novotny-Farkas F., Allmaier G.: Impact of engine oil degradation on wear and corrosion caused by acetic acid evaluated by chassis dynamometer bench tests. Wear 2014;317:64-76

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Dörr N., **Besser C.**, Pisarova L., Hunger H., Litzow U., Orfaniotis A.: Bio-diesel fuel alteration and analysis. 19th International Colloquium Tribology, January 21st to 23th 2014, Esslingen, Germany

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